The Effect of Electronegative Substituents on the Reductive Dimerization of Schiff Bases. Formation of Vicinal Dianions

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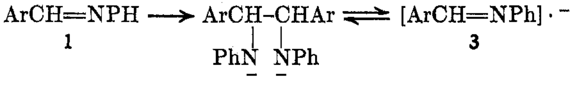
Received March 14, 1973

Reduction of *N*-(*p*-cyanobenzal)aniline by sodium metal in tetrahydrofuran produces initially the expected dimers which later dissociate as the radical anion is further reduced to a monomeric dianion. Alkylation and acylation of this dianion are described and similar observations are reported for *N,N'*-diphenylterephthalaldimine. The formation of the monomeric dianions is attributed to the stabilization of the radical anion which facilitates dissociation of the dimeric dianions initially formed and permits further reduction to occur. Analogies between these reductions and the electrochemical behavior of Schiff bases is noted.

When substituted *N*-benzalanilines, **1**, are dimerized by alkali metals in aprotic solvents,[1-4] an isomerization of the diastereomeric dimeric dianions,[3-4] **2**, is observed under certain reaction conditions. This isomerization has been traced[4] to an equilibrium between the dimeric dianion, **2**, and the radical anion **3**



$$\underset{\mathbf{1}}{\text{ArCH=NPH}} \longrightarrow \underset{\mathbf{2}}{\text{ArCH}(\overset{-}{\text{N}}\text{Ph})\text{–CH}(\overset{-}{\text{N}}\text{Ph})\text{Ar}} \rightleftharpoons \underset{\mathbf{3}}{[\text{ArCH=NPh}]\cdot^{-}}$$

which permits the original kinetic product to assume its more thermodynamically stable composition.

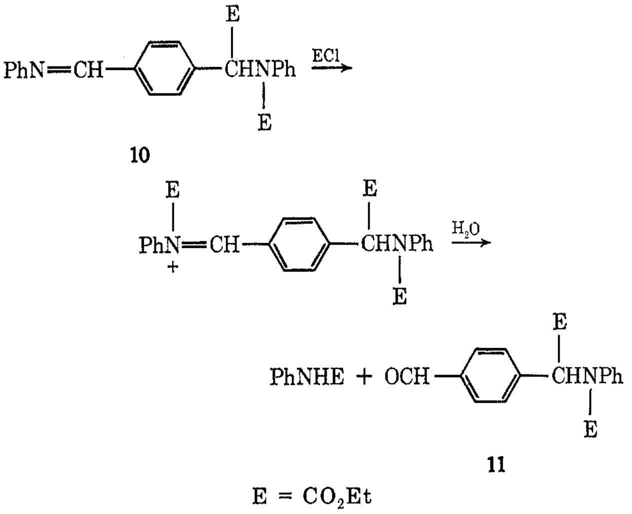
Substituents have a detectable effect on the isomerization but, with one exception, only electropositive substituents have been examined. The exception (**1**, Ar = *m*-ClC_6H_4) showed a marked increase in the rate of isomerization reflecting stabilization of the corresponding radical anion. Further studies of the *o*- and *p*-chloro analogs were frustrated by reductive dehalogenation of their radical anions.[5] However, the behavior of the *m*-chloro compound prompted an examination of other electronegative substituents with the consequences reported here.

The Schiff base *N*-(*p*-cyanobenzal)aniline (**4**, Y = CN) reacted rapidly with sodium in tetrahydrofuran (THF) and attained an equilibrium uptake of 2 g-atoms of sodium per 1 mol in 4 hr. Protonation of this reaction mixture produced the dimeric diamine **5** (Y = CN) and the monomeric amine **6** (Y = CN) but their relative proportions depended on the duration of the reaction, the amount of dimer decreasing as the reduction continued. This suggested that the ultimate product generated by the reduction was a monomeric dianion **7**.

The existence of **7** was established by alkylating the organometallic compound with methyl iodide and 1,3-diiodopropane and by acylating with ethyl chloroformate to form, respectively, **8**, **9**, and **10** (Y = CN), as outlined in Scheme I. In general, this chemical behavior resembled that of the well-known dianion derived from benzophenone anil by alkali metal reduction.[1,6]

A search for additional electronegative substituents showed that a *p*-carbomethoxy group was unsatisfactory,[7] but a second aldimine group provided analogous results. *N,N'*-Diphenylterephthalaldimine (**4**, Y = PhN=CH–) also was reduced to a dianion and products **8**, **9**, and **10** (Y = PhN=CH) were generated by alkylation and acylation. Isolation of **10** (Y = PhN=CH) was unsuccessful because of its easy hydrolysis and oxidation.

By taking advantage of the ready hydrolysis of these imines, the substituted benzaldehyde **11** was isolated. Indeed, in one instance when excess chloroformate was used, hydrolysis occurred during normal aqueous work-up, reflecting the increased hydrolytic sensitivity of the probable intermediate iminium salt.[8]



Rather surprisingly, the isomeric bisaldimine, *N,N'*-dibenzal-*p*-phenylenediamine (**12**), was also reduced to a dianion by sodium. Protonation produced *N,N'*-dibenzylquinone diimine, but as yet resolution of the air-sensitive diastereomeric mixtures produced on alkylation has not been successful.

Qualitatively, the stabilization of radical anions by

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[1] (a) W. Schlenk, J. Apprenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914); (b) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 281 (1928); M. Szwarc, *Accounts Chem. Res.*, **5**, 169 (1972), and V. Kalyanaraman and M. V. George, *J. Organometal. Chem.*, **47**, 225 (1973), present comprehensive reviews of the interaction of alkali metals with unsaturated compounds.

[2] J. J. Eisch, D. D. Kaska, and C. J. Peterson, *J. Org. Chem.*, **31**, 453 (1966).

[3] J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2497 (1966).

[4] J. G. Smith and I. Ho, *J. Org. Chem.*, **37**, 653 (1972).

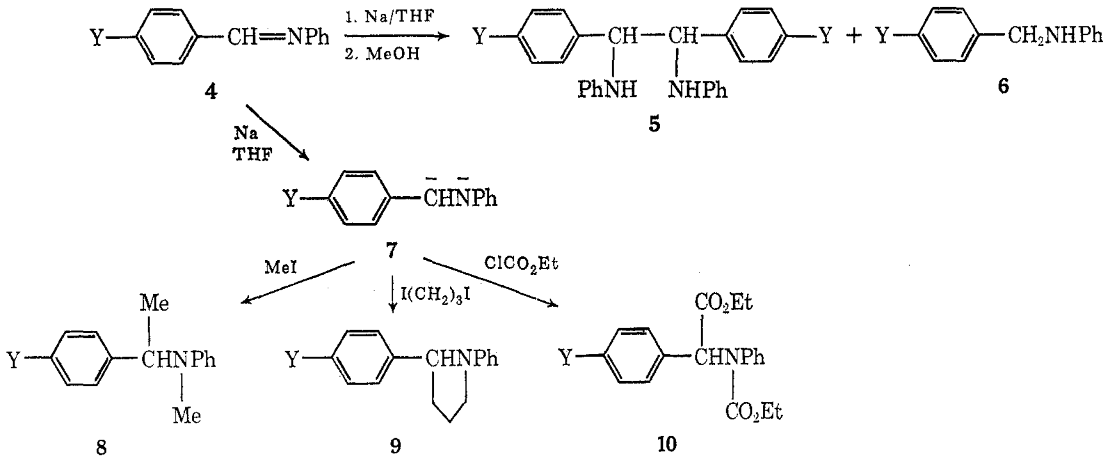
[5] J. G. Smith and I. Ho, *J. Org. Chem.*, **37**, 4260 (1972).

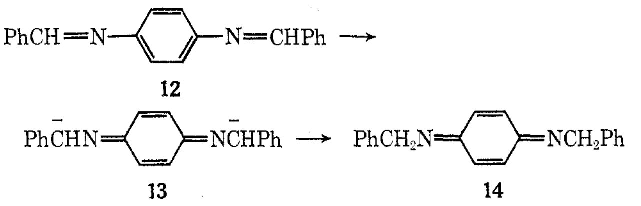
[6] (a) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2245 (1966); (b) J. G. Smith and R. A. Turle, *J. Org. Chem.*, **37**, 126 (1972).

[7] No methyl groups could be detected in the crude reaction product, suggesting that extensive reduction and/or condensation reactions had occurred.

[8] (a) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, p 403. (b) The ethyl *N*-phenylcarbamate was also isolated.

SCHEME I
REACTIONS OF THE VICINAL DIANION





electronegative substituents has been noted[9] in the reduction of substituted benzenes with alkali metals. Quantitatively, electrochemical reductions illustrate this nicely. For example, the half-wave reduction potentials of substituted benzophenones[10] become less negative as the substituent group increases in electronegativity. Similar observations[11] have been made for a variety of Schiff bases and relationships between the half-wave reduction potential and Hammett σ constants were noted.

Undoubtedly, the substituent effects a decrease in the energy of the lowest unoccupied molecular orbital,[12] facilitating both the electron transfer as well as the delocalization of the charge density in the generated radical anion.[13]

The nitrile group is a particularly interesting substituent, causing a marked change in the half-wave reduction potential[11a] commensurate with its strong electronegative character. However, while exerting an activating influence it is not itself reduced.[14]

Frequently, second one-electron reductions are observed in these electrochemical reactions and in general the behavior of these second waves resembles that of the first. The second wave is attributed to a reduction of the initially formed radical anion to a dianion (provided aprotic anhydrous solvents are used) in the manner suggested for hydrocarbons.[15]

It is readily apparent that the alkali metal reductions closely parallel the electrochemical observations. Stabilization of the radical anion by the electronegative substituent permits facile dissociation of the dimeric dianions initially formed as well as further reduction to the monomeric dianion. Since protonation of the latter by the reaction medium is slow, further chemical transformations of this dianion can be effected.

Considering the extensive delocalization[16] of the anionic charge in the conjugated systems, it is perhaps surprising that the reactions are not more complex. Indeed, the behavior of **7** (Y = PhN=CH) and **13**, where the electronegative nature of nitrogen failed to direct the reaction to a quinonedimethide product in the case of the former or to a reaction at only one of the imine groups in the latter,[17] leads us to suggest a stepwise alkylation. The less delocalized "terminal" anionic center reacts first, forming an ambident, highly delocalized anion which reacts fastest at its most reactive site, the carbanionic end, *i.e.*, Scheme II.

Experimental Section

Melting points are uncorrected and were determined in open capillaries with a Mel-Temp apparatus. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer and nmr spectra on a Varian T-60 spectrometer. Chemical shifts are in parts per million downfield from internal tetramethylsilane (δ scale). Silica gel (0.05–0.2 mm) purchased from E. Merck AG was used for column chromatography and Eastman Chromagram 6060 (silica gel) sheets were used for thin layer chromatography (tlc). Analyses were determined by M-H-W Laboratories, Garden City, Mich.

The purification of solvents, the reaction of the imines with alkali metals, and the handling of the organometallic compounds have been described[4] elsewhere.

p-Cyanobenzaldehyde was prepared in 49% yield by the chromium trioxide oxidation of *p*-tolunitrile, the procedure being

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(9) J. J. Eisch, *J. Org. Chem.*, **28**, 707 (1963).

(10) P. Zuman, O. Oxner, R. F. Rekker, and W. Th. Nauta, *Collect. Czech. Chem. Commun.*, **33**, 3213 (1968).

(11) (a) L. V. Kononenko, V. D. Bezuglyi, and V. N. Dmitrieva, *J. Gen. Chem. USSR*, **38**, 2087 (1968); (b) V. N. Dmitrieva, N. A. Rozanel'skaya, L. V. Kononenko, B. I. Stepanov, and V. D. Bezuglyi, *ibid.*, **41**, 57 (1971), and references cited therein; (c) V. N. Dimitrieva, N. I. Mal'tseva, V. D. Bezuglyi, and B. M. Krasovitskii, *ibid.*, **37**, 347 (1967); (d) J. M. W. Scott and W. H. Jura, *Can. J. Chem.*, **45**, 2375 (1967); (e) P. Martinet, J. Simonet, and J. Tendil, *C. R. Acad. Sci., Ser. C*, **268**, 303 (1969).

(12) In this respect, approximate molecular orbital calculations by Scott and Jura[11d] are of interest.

(13) K. W. Bowers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 211.

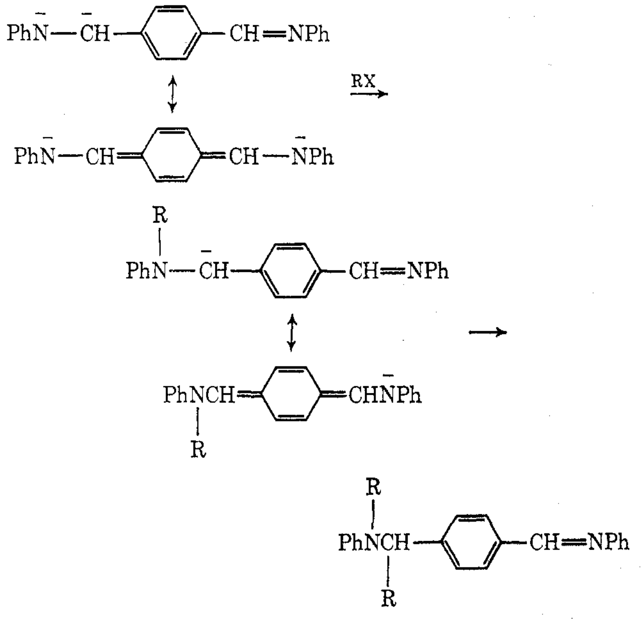
(14) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 743 (1969). (b) Provided conditions leading to protonation of the nitrile are avoided: P. Zuman and O. Manousek, *Collect. Czech. Acad. Sci.*, **34**, 1580 (1969).

(15) (a) H. A. Laitinen and S. Wawzonek, *J. Amer. Chem. Soc.*, **64**, 1765 (1942). (b) G. J. Hoytink in "Advances in Electrochemistry and Electrochemical Engineering," Vol. 7, P. Delahay and C. W. Tobias, Ed., Interscience, New York, N. Y., 1970, p 221.

(16) For the sake of brevity, we have represented the dianion by the structure most resembling the products, and the counterions have been omitted.

(17) Essentially the exact opposite was observed.

SCHEME II



the same as that used[18] for the preparation of *p*-nitrobenzaldehyde.

N-(*p*-**Cyanobenzal)aniline.**—Aniline (9.3 g, 0.1 mol) was added dropwise to a stirred solution of *p*-cyanobenzaldehyde at 80°. After 6 hr the solution was cooled, and the product, which precipitated, was recrystallized twice from ethanol to give 17.0 g (82% yield), mp 89–91°.

Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.55; H, 4.89; N, 13.59. Found: C, 81.35; H, 5.03; N, 13.42.

N,*N*′-**Diphenylterephthalaldimine (4, Y = PhN=CH)** was prepared by the same procedure in 82% yield,[19] mp 159–160°.

N,*N*′-**Dibenzal-*p*-phenylenediamine (12)** was prepared[20] in 91% yield, mp 138–140° (reported[20] mp 138°).

Reductive Dimerization of *N*-(*p*-Cyanobenzal)aniline (4, Y = CN).—The results of a time study in the case of 4 (Y = CN) are summarized in Table I. Individual products were isolated from separate experiments as described below. Attempts to effect a reductive metalation of 4 (Y = CN) with sodium in diethyl ether were not successful.

TABLE I

PRODUCT COMPOSITION IN THE REDUCTION OF *N*-(*p*-CYANOBENZAL)ANILINE BY SODIUM IN THF

Time, hr	g-atoms of Na per mol of 4 (Y = CN)^a	Product composition,^{a} %		
		5 (Y = CN)		6
		Racemic	Meso	(Y = CN)
0.5	0.20	69	31	Trace
1.0	0.73	62.5	18.8	18.8
2.0	1.36	34.2	9.8	56.0
4.0	1.95	7.7	Trace	92.3
8.0	2.05	~2.5	Trace	97.5
24.0	2.08	~2.5	Trace	97.5

[a] Analysis by nmr. Unreacted 4 (Y = CN) is omitted.

Isolation of *rac*-1,2-Di(*p*-cyanophenyl)-*N*,*N*′-diphenylethylenediamine (5, Y = CN).—The standard preparative run consisted of 2.06 g (0.01 mol) of *N*-(*p*-cyanobenzal)aniline, 100 ± 10 ml of THF, and 1.8 g (0.08 g-atom) of sodium in a Schlenk tube. After shaking for 2 hr, the solution (deep red) was drained from the excess metal into a nitrogen-filled flask, cooled to −60°, and treated with 2 ml of methanol.

After diluting with water, the crude reaction product (2.08 g) was isolated by ether extraction and chromatographed on 80 g of silica gel with benzene as eluent. The first fraction, 0.36 g (18% yield), was *N*-(*p*-cyanobenzyl)aniline, mp and mmp with an authentic sample 84–86°.

The second fraction, 1.16 g (80% yield), crystallized on standing. Recrystallization from ether provided an analytical sample of *rac*-5 (Y = CN): mp 165–168°; ir (KBr) 3440 (NH), 2240 (CN), 1600, 1510, 1320, 850, 755, 695 cm^{-1} (aromatic CH); nmr ($CDCl_3$) δ 4.51 (s, 2, benzylic H), 6.03–7.60 (m, 18, aromatic H).

Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.14; H, 5.35; N, 13.52. Found: C, 80.91; H, 5.38; N, 13.33.

The meso isomer[21] has not yet been isolated but the nmr spectrum of the crude dimer showed a benzylic proton singlet at δ 5.03.

Isolation of *N*-(*p*-Cyanobenzyl)aniline (6, Y = CN).—A standard preparative run (6 hr reaction time) was treated as described above. The crude reaction product (2.01 g) was recrystallized three times from ethanol, 1.83 g (91% yield) of 6 (Y = CN): mp 86–87°; ir (Nujol) 3440 (NH), 2240 (CN), 1600, 1510, 810, 755, 690 cm^{-1} (aromatic CH); nmr ($CDCl_3$, D_2O washed), 4.45 (s, 2, CH_2), 6.5–7.4 (m, 5, C_6H_5N), 7.58 (q, 4, J = 9 Hz, $-C_6H_4CN$).

Anal. Calcd for $C_{14}H_{12}N_2$: C: 80.72; H, 5.81; N, 13.45. Found: C, 80.90; H, 5.92; N, 13.55.

Preparation of *p*-[1-(*N*-Methylanilino)ethyl]benzonitrile (8, Y = CN).—A standard preparative run (6 hr reaction time) was drained from excess sodium, cooled to −60°, and treated with 2.82 g (0.02 mol) of methyl iodide. After 2 hr of stirring at −60°, the reaction was warmed to room temperature overnight and diluted with water and the reaction product (2.10 g) was isolated by ether extraction. Chromatography on 80 g of silica gel with benzene as eluent provided one major fraction, 1.89 g (90% yield) of 8 (Y = CN) as a yellow oil: bp 158–159° (0.13 mm); ir (film) 2210 (CN), 1600, 1500, 830, 740, 680 cm^{-1} (aromatic CH); nmr ($CDCl_3$) δ 1.56 (d, 3, J = 7 Hz, CH_3CH), 2.72 (s, 3, NCH_3), 5.23 (q, 1, J = 7 Hz, CH_3CH), 6.6–6.7 (m, 9, aromatic CH).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.51; H, 6.70; N, 12.10.

Preparation of 2-(*p*-Cyanophenyl)-1-phenylpyrrolidine (9, Y = CN).—The above reaction was repeated using 2.96 g (0.01 mol) of 1,3-diiodopropane in place of the methyl iodide. Chromatography again provided 2.15 g (87% yield) of 9 (Y = CN) as a viscous yellow oil: bp 174–177° (0.08 mm); ir (film) 2220 (CN), 1600, 1510, 830, 740, 690 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 1.8–2.6 (m, 4, $CH_2CH_2CH_2N$), 3.2–3.9 (m, 2, $CH_2CH_2CH_2N$), 4.75 (q, 1, J_A = 8 Hz, J_B = 2 Hz, $CHCH_AH_B$), 6.3–7.7 (m, 9, aromatic H).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.07; H, 6.62; N, 11.06.

Preparation of Ethyl *α*-(*N*-Carbethoxyanilino)-*p*-cyanophenylacetate (10, Y = CN).—The above reaction was repeated using 2.17 g (0.02 mol) of ethyl chloroformate instead of the alkyl iodide. The crude product, 2.48 g of a red oil, was chromatographed on 120 g of silica gel with benzene as eluent to give 0.81 g (33% yield) of ethyl *α*-anilino-*p*-cyanophenylacetate: bp 189–192° (0.08 mm); ir (film) 3400 (NH), 2210 (CN), 1730 (C=O), 1600, 1500, 740, 680 (aromatic CH), 1010 cm^{-1} ($-CO_2-$); nmr ($CDCl_3$, D_2O washed) δ 1.20 (t, 3, J = 7 Hz, CH_3CH_2), 4.22 (q, 2, J = 7 Hz, CH_3CH_2), 5.13 (s, 1, benzylic H), 6.5–7.3 (m, 5, C_6H_5N), 7.67 (s, 4, $-C_6H_4CN$).

Continuing the elution with chloroform gave the main fraction, a solid which after recrystallization from ethanol amounted to 1.28 g (52% yield) of 10 (Y = CN): mp 85–86°; ir (film) 2215 (CN), 1740 and 1700 (C=O), 1600, 1490, 760, 690 (aromatic CH), 1020 and 1040 cm^{-1} (CO_2); nmr ($CDCl_3$) δ 1.23 (q, 6, J = 7 Hz, CH_3CH_2), 4.27 (pentet, 4, J = 7 Hz, CH_3CH_2), 5.83 (s, 1, benzylic H), 7.1–7.7 (m, 9, aromatic H).

Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.07; H, 5.92; N, 7.92.

Preparation of *N*-(*p*-Anilinomethylbenzal)aniline (6, Y = PhN=CH).—The standard preparative run consisted of 1.42 g (0.005 mol) of 4 (Y = PhN=CH) and 1.8 g (0.08 g-atom) of sodium in 100 ± 10 ml of THF shaken for 24 hr in a Schlenk tube. The deep purple solution was drained from the excess alkali metal into a nitrogen-filled flask, cooled to −60°, and treated with 2 ml of methanol. The solution immediately became orange and, after warming to room temperature and diluting with water, the

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[18] (a) S. V. Lieberman and R. Connor, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 441; (b) O. Schales and H. A. Graefe, *J. Amer. Chem. Soc.*, **74**, 4489 (1952).

[19] W. Steinkopf, R. Leitsmann, A. H. Müller, and H. Wilhelm, *Justus Liebigs Ann. Chem.*, **541**, 260 (1939), report mp 159°.

[20] A. Ladenburg, *Chem. Ber.*, **11**, 599 (1878).

[21] The stereochemical assignments are based on the assumptions described earlier.[4]

product was isolated by ether extraction. Recrystallization from ethanol gave 1.3 g (90% yield) of **6** (Y = Ph N=CH–): mp 94–96°; ir (KBr) 3400 (NH), 1635 (C=N), 1610, 1510, 830, 760, 700 cm^{-1} (aromatic CH); nmr ($CDCl_3$) δ 4.1 (broad s, 1, NH), 4.38 (s, 2, benzylic H), 6.5–8.0 (m, 14, aromatic H), 8.45 (s, 1, CH=N).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.83; H, 6.33; N, 9.88. Found: C, 83.89; H, 6.29; N, 9.85.

Preparation of *N*-*p*-[1-(*N*-Methylanilino)ethyl]benzalaniline (8, Y = PhN=CH).—The above reaction was repeated using 1.42 g (0.01 mol) of methyl iodide in place of the methanol. After the solution was warmed to room temperature for 12 hr, the crude product was isolated by ether extraction and recrystallized from hexane, 1.42 g (90% yield) of **8** (Y = PhN=CH): mp 70–72°; ir (KBr) 1630 (C=N), 1590, 1500, 830, 730, 680 cm^{-1} (phenyl); nmr (C_6D_6) 1.22 (d, 3, J = 7 Hz, CH_3CH), 2.40 (s, 3, NCH_3), 4.88 (q, 1, J = 7 Hz, $CH_3\mathbf{CH}$), 6.7–8.0 (m, 14, aromatic H), 8.27 (s, 1, CH=N).

Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.05; H, 7.05; N, 8.92. Found: C, 84.19; H, 7.06; N, 9.04.

Preparation of *N*-*p*-[2-(1-Phenylpyrrolidinyl)]benzalaniline (9, **Y = PhN=CH**).—The above reaction was repeated using 1.48 g (0.005 mol) of 1,3-diiodopropane in place of the methyl iodide. Decolorization took place within 2 min at −60°. After 24 hr at room temperature, the product (oil, 1.50 g) was isolated and chromatographed on 60 g of silica gel with benzene as eluent. The major fraction, 1.2 g (80% yield), was recrystallized from ethanol to give an analytical sample of 9 (Y = PhN=CH): mp 132–135°; ir (KBr) 1630 (C=N), 1590, 1500, 770, 750, 700 cm^{-1} (aromatic CH); nmr ($CDCl_3$) δ 1.8–2.7 (m, 4, $CH_2\mathbf{CH_2}$-CH_2N), 3.2–4.0 (m, 2, $CH_2CH_2\mathbf{CH_2}N$), 4.82 (broad d, 1, J = 6 Hz, benzylic H), 6.3–8.0 (m, 15, aromatic H), 8.47 (s, 1, CH=N).

Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.65; H, 6.80; N, 8.59. Found: C, 84.47; H, 7.01; N, 8.57.

Preparation of *p*-(α,*N*-Dicarbethoxyanilinomethyl)benzaldehyde (11).—The above reaction was repeated using 1.09 g (0.01 mol) of ethyl chloroformate in place of alkyl iodide. Decolorization to a deep orange occurred in 20 min at −60°. After 24 hr at room temperature, the crude product was diluted with 200 ml of ether. The solution was filtered (NaCl) and solvent was evaporated, leaving a crude yellow oil which was hydrolyzed with 1.0 ml of HCl in 100 ml of ether for 12 hr. After diluting with more ether, washing with water, and drying, the solvent was evaporated. The residue was recrystallized from methanol to give **11**, 1.25 g (70% yield): mp 72–74°, ir (Nujol) 1740 (aldehyde CO), 1700 and 1685 (ester CO), 1590, 1490, 780, 730, 700 (aromatic CH), 1200 cm^{-1} (CO_2); nmr ($CDCl_3$) δ 1.22 (q, 6, J = 7 Hz, $\mathbf{CH_3}CH_2$), 4.25 (pentet, 4, J = 7 Hz, both CH_3-$\mathbf{CH_2}$), 5.90 (s, 1, benzylic H), 7.17 (s, 5, C_6H_5N), 7.37 and 7.77 (AB q, 4, J = 8 Hz, $-C_6H_4-$), 10.05 (s, 1, CHO).

Anal. Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96, N, 3.94. Found: C, 67.63; H, 5.96; N, 3.82.

When the reaction was repeated with an excess (2.1 g, 0.02 mol) of ethyl chloroformate, hydrolysis occurred during an aqueous work-up. The crude product (an oil, 2.0 g) was distilled to give 1.2 g (60% yield), bp 99–102° (0.6 mm), which solidified, mp 46–47.5°, undepressed on admixture with ethyl *N*-phenylcarbamate. The pot residue from the distillation crystallized on digestion with a small amount of methanol. The solid, 0.5 g (25% yield), mp 72.5–74°, was identified as **11** by mixture melting point.

Preparation of *N*,*N*′-Dibenzylquinonediimine (14).—The reduction of **12** (0.005 mol) by sodium metal in THF followed the same procedure as the reduction of **4** (Y = PhN=CH). The dark brown solution of the organosodium compound was quenched with 2 ml of methanol at room temperature. The crude product was isolated by ether extraction of the water-diluted reaction mixture and recrystallized from hexane under nitrogen to give 1.21 g (85% yield) of **14**: mp 95.5–97°; ir (KBr) 1520, 1470, 1450, 1400, 1290, 810, 735, 695 cm^{-1}; nmr (C_6D_5) δ 3.27 (s, 4, CH_2), 5.70 (s, 4, vinyl H), 6.47 (broad s, 10, aromatic H).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.87; H, 6.33; N, 9.78. Found: C, 83.65; H, 6.41; N, 9.73.

Acknowledgment.—This research was financially supported by the National Research Council of Canada.

Registry No.—**4** (Y = CN), 22257-39-2; **4** (Y = PhN=CH), 14326-69-3; *rac*-**5** (Y = CN), 40577-01-3; *meso*-**5** (Y = PhN=CH), 40577-02-4; **6** (Y = CN), 37812-49-0; **6** (Y = PhN=CH), 40577-04-6; **8** (Y = CN), 40577-05-7; **8** (Y = PhN=CH), 40577-06-8; **9** (Y = CN), 40577-07-9; **9** (Y = PhN=CH), 40577-08-0; **10** (Y = CN), 40577-09-1; **11**, 40577-10-4; **12**, 797-20-6; **14**, 40577-12-6; aniline, 62-53-3; *p*-cyanobenzaldehyde, 105-07-7; *N*-(*p*-formylbenzal)aniline 40577-14-8; ethyl α-anilino-*p*-cyanophenylacetate, 40577-15-9.

Kinetics of the Autoxidation of Diisopropylbenzenes and Derivatives

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Received December 29, 1972

The oxidation of meta- and para-substituted isopropylbenzenes with molecular oxygen has been studied kinetically in chlorobenzene at 60°, using azobisisobutyronitrile as an initiator. The rate constants are in a range of 5.58×10^{-3} to 2.22×10^{-3} (mol sec)$^{-1/2}$ and decrease in the order *p*-diisopropylbenzene > *p*-isopropylcumyl hydroperoxide > *m*-diisopropylbenzene > isopropylbenzene > *m*-isopropylcumyl hydroperoxide > *m*-isopropylacetophenone > *m*-isopropylcumyl alcohol > *p*-isopropylacetophenone > *p*-isopropylcumyl alcohol. The observed relative rates fit Hammett's equation, giving a ρ value of −0.50 (r = 0.955). The plot and the observed relative rates give $\sigma_p = -0.14$ and $\sigma_m = 0.06$ for $-C(CH_3)_2OOH$, $\sigma_p = 0.60$ and $\sigma_m = 0.47$ for $-C(CH_3)_2$-OH. These substituent effects are discussed in terms of electronic theory.

The autoxidation of *m*- and *p*-diisopropylbenzenes (DIB) to give the corresponding dihydroperoxides has been studied to obtain information on the preparation of resorcinols (from *m*-DIB) and hydroquinones (from *p*-DIB) by acid-catalyzed decomposition of their hydroperoxides.[1-3] The maximum yields of dihydroperoxides in the autoxidation was *ca.* 10%, because dihydroperoxides, once formed, may pyrolyze, resulting in the formation of ketones and alcohols. The autoxidation of DIB may proceed according to Scheme I in analogy with other autoxidation of alkylbenzene.[4,5]

The meta isomer would analogously give the corresponding compounds: (**1**) diisopropylbenzene; (**2**) isopropylcumyl hydroperoxide; (**3**) isopropylcumyl alcohol; (**4**) isopropylacetophenone; (**5**) bis(2-hydroperoxy-2-propyl)benzene; (**6**) bis(2-hydroxy-2-propyl)benzene; (**7**) acetylcumyl hydroperoxide. Isopropylcumyl alcohols **3** and isopropylacetophenones **4** are formed by the decomposition of diisopropyl-

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[1] Distillers Co. Ltd., British Patent 641,250 (1950).

[2] Distillers Co. Ltd., British Patent 646,102 (1950).

[3] Distillers Co. Ltd., British Patent 982,515 (1965).

[4] T. G. Traylor and G. A. Russell, *J. Amer. Chem. Soc.*, **87**, 3698 (1965).

[5] H. S. Blanchard, *J. Amer. Chem. Soc.*, **81**, 4548 (1959).