Reductive Dehalogenations by Alkali Metals and Sodium Naphthalenide. Capture of Solvent-Derived Intermediates

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o-Chlorobenzylideneaniline (1) was treated with sodium and lithium in diethyl ether (DEE) and tetrahydrofuran (THF) and with sodium naphthalenide in THF. Dehalogenation occurred, and the intermediate solvent-derived species were captured by the aldimine group of 1 and its chlorine-free analog *N*-benzylideneaniline. The reaction products were isolated, their structures were established, and the reaction was interpreted as proceeding through carbanions formed by removal of the α hydrogen from the ether solvents. Results of experiments performed in mixed solvents support this interpretation.

Recently, the dehalogenation of alkyl and aryl halides has been the subject of considerable discussion.[1–6] Two mechanisms[7] have been advanced for this reaction, both requiring the solvent to supply the proton which replaces the lost halogen. The subsequent solvent-derived species are highly reactive, and their existence has been inferred[8] largely on the basis of their decomposition products.

Our interest in the dehalogenation reaction stems from the possibility of trapping these solvent-derived intermediates before they decompose. If successful, such a reaction would provide direct chemical evidence for the generation of these intermediates and afford a possible access to a variety of reactive intermediates which are not easily accessible[9] even under ideal circumstances.

Drawing upon our earlier study[10] of the reductive dimerization of substituted aryl imines, *N*-(*o*-chlorobenzylidene)aniline (1) was chosen as the aryl halide to be examined. To keep the reaction as simple as possible, the radical anion was generated *in situ* from the imine and sodium metal. Thus 1 not only served as the aryl halide undergoing dehalogenation but also provided the functional group to capture the reactive intermediates arising from the solvent.

Results

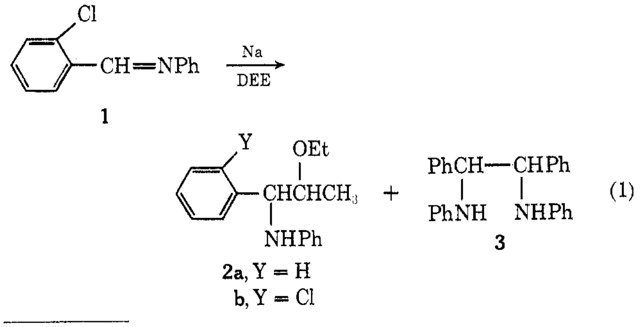
In diethyl ether (DEE), *N*-(*o*-chlorobenzylidene)aniline (1) reacted slowly with sodium. Titration of aliquot samples of the reaction mixture showed an apparent equilibrium uptake of 1 g-atom of sodium/mol of 1. The nmr spectrum of the crude reaction product indicated clearly the presence of chemically bound solvent in some component of the reaction mixture.

Fortunately, one component crystallized readily from ether, and chemical analyses and mass spectra established the molecular formula as $C_{17}H_{20}NCl$. The presence of an amino group was established by the ir spectrum while the nmr spectrum could only be interpreted as due to *N*-phenyl-1-(*o*-chlorophenyl)-2-ethoxypropylamine (**2b**). Thus the methyl region consisted of a superimposed doublet and triplet indicating that reaction had occurred at the α position of DEE, while the benzylic proton was a doublet showing that this was the point of attachment of the moiety from DEE. In addition, the mass spectrum showed the principal fragmentation to be the loss of this DEE-derived moiety to give the Cl-isotopic fragment pair *m/e* 218 and 216.

Gas chromatography disclosed the presence of four volatile compounds[11] in the crude reaction mixture with one having a retention time identical with that of the isolated diastereomer of **2b**.

On a preparative scale, only the third and fourth peaks were separately isolated, and these proved to be the erythro and threo isomers of **2b**. The first and second peaks were collected together, and spectral and analytical data established this as a mixture of the *erythro*- and *threo*-*N*,1-diphenyl-2-ethoxy-1-propylamines, **2a**.

Comparing the nmr spectra of these isolated materials with that of the crude reaction mixture disclosed that the benzylic proton region (δ 4–5 ppm) contained two sharp singlets in addition to the four doublets corresponding to the benzylic protons of erythro and threo **2a** and **2b**. These singlets had the same chemical shifts[12] as the *N*,*N'*,1,2-tetraphenylethylenediamines (**3**). The *meso*-**3** was isolated from the reaction mixture by means of its DMF complex.[13] Thus the overall



1

2a, Y = H
b, Y = Cl

3

(1)

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[1] J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971), and references cited therein.

[2] G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

[3] T. C. Cheng, L. Headley, and A. F. Halasa, *J. Amer. Chem. Soc.*, **93**, 1502 (1971).

[4] W. Adam and J. Arce, *J. Org. Chem.*, **37**, 507 (1972).

[5] S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4581 (1971).

[6] W. C. Danen, T. J. Tipton, and D. G. Saunders, *J. Amer. Chem. Soc.*, **93**, 5186 (1971).

[7] A third has been suggested, M. Schlosser, G. Heinz, and L. V. Chau, *Chem. Ber.*, **104**, 1921 (1971), but not substantiated by experimental data.

[8] (a) R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, **37**, 560 (1972); (b) S. C. Honeycutt, *J. Organometal. Chem.*, **29**, 1 (1971); (c) A. Maercker and W. Theysohn, *Justus Liebigs Ann. Chem.*, **747**, 70 (1971); (d) T. J. Wallace and R. J. Gritter, *Tetrahedron*, **19**, 657 (1963); (e) A. Rembaum, S-P. Siao, and N. Indictor, *J. Polym. Sci.*, **56**, S17 (1962); (f) B. Angelo, *Bull. Soc. Chim. Fr.*, 1091 (1966).

[9] (a) U. Schöllkopf, H. Küppers, H.-J. Traenckner, and W. Pitteroff, *Justus Liebigs Ann. Chem.*, **704**, 120 (1967); (b) B. Castro, *Bull. Soc. Chim. Fr.*, 1533, 1540, 1547 (1967); (c) J. Vollléras, *Organometal. Chem. Rev. A*, **7**, 81 (1971).

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

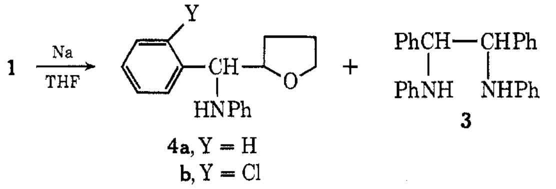
[11] A fifth, *N*-benzylideneaniline, was observed in reactions which were incomplete.

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

[13] R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956); *ibid.*, **43**, 2029 (1960).

reaction is that shown in eq 1 and integration of the nmr spectrum in the benzylic proton region provided an analysis of the reaction mixture. That this analysis accounted for essentially all the reaction products was supported by the correspondence shown between the ionic chloride formed during the reaction and that calculated from the measured product composition.

In the more basic solvent tetrahydrofuran (THF), the same type of product mixture was formed (see eq 2). However, as expected[10,12,14] the dimer **3** was



(2)

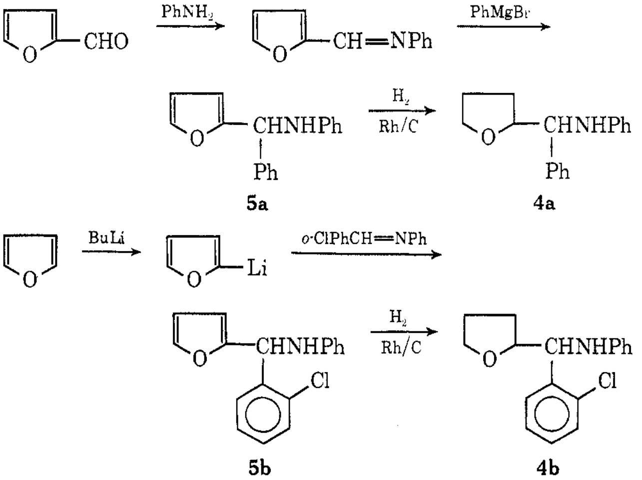
3

4a, Y = H
b, Y = Cl

chiefly the racemic diastereomer. In this reaction, the products **4** were isolated by column chromatography and had sufficiently complex nmr spectra that their structures were verified by synthesis.

The synthetic routes are shown in Scheme I. Different routes were required for **4a** and **4b** since the reaction between the Grignard reagent and *N*-(furfurylidene)aniline used in the preparation of **4a** failed when adapted to the preparation of **4b**.

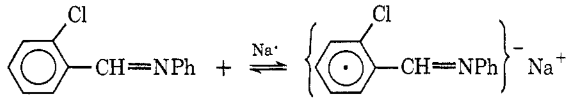
SCHEME I
PREPARATION OF *N*-(ARYLTETRAHYDROFURYLMETHYL)ANILINE



To confirm the original supposition that the reaction between **1** and alkali metals corresponded to that between **1** and the radical anion of naphthalene, the latter reaction was also examined. In THF, the same spectrum of products was produced but the reaction proceeded rapidly even at −60°. Undoubtedly, the reaction was greatly facilitated[15] by the much higher concentration of the reducing agent (sodium naphthalenide) in solution.

Discussion

Sargent[2] has cogently summarized the evidence supporting the suggested mechanisms for the dehalogenation of aryl halides and radical anions. Adapting his conclusions to the present reaction leads to the following sequence. The initially formed radical anion (reaction 3) eliminates a halide ion in the rate-limiting[16a] reaction 4.



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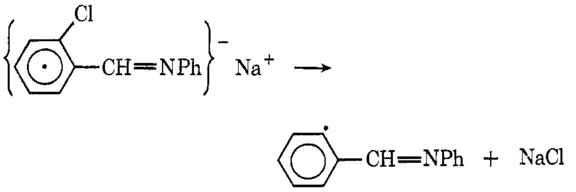

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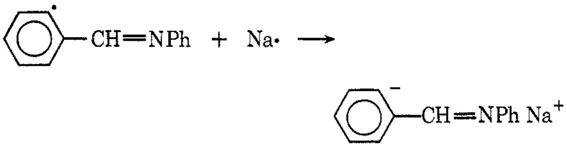

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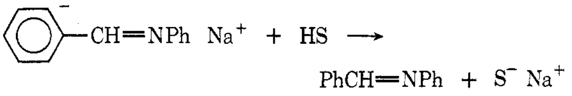

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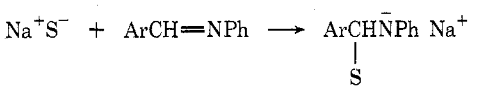
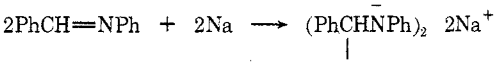


$$\mathrm{Na^+S^-} + \mathrm{ArCH{=}NPh} \longrightarrow \mathrm{Ar\underset{\displaystyle S}{\underset{|}{C}}H\bar{N}Ph\ Na^+} \qquad (7)$$



$$\mathrm{2PhCH{=}NPh} + 2\mathrm{Na} \longrightarrow \mathrm{(Ph\underset{|}{C}H\bar{N}Ph)_2\ 2Na^+} \qquad (8)$$

The aryl radical so formed is reduced (reaction 5) to an aryl anion by the alkali metal as shown or equally likely by the radical anion formed in reaction 3. Abstraction of an α hydrogen from the ether solvent (HS) generates the chlorine-free Schiff base and the solvent derived anion in reaction 6. This last anion then adds to either of the two Schiff bases present in solution (reaction 7) while the *N*-benzylideneaniline also undergoes a competitive dimerization[10,12,14,16b] (reaction 8).

The extreme rapidity of electron-transfer reactions[17] dictates the formation of anionic intermediates. The fact that the nucleophilic addition reaction 7 successfully competes with reaction 8, also an electron-transfer reaction, is best explained by noting that the solvent anion is formed in the immediate vicinity of the substrate with which it reacts. It is this spatial proximity which permits addition of the solvent anion to compete. Even so, the addition reaction can be completely surpressed by using an excess of the more efficient reducing reagent, sodium naphthalenide (3 mol/mol of **1**). Reaction 8 then becomes dominant over 7 and the reaction products consist only of dimeric dianions.[18]

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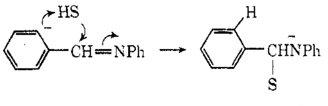
[14] J. J. Eisch, D. D. Kaska, and C. J. Peterson, *J. Org. Chem.*, **31**, 453 (1966).

[15] J. J. Eisch, *ibid.*, **28**, 707 (1963).

[16] (a) The formation of products from both **1** and *N*-benzylideneaniline is the basis for this. (b) A referee has suggested the attractive possibility that reactions 6 and 7 may be a one-step addition involving a cyclic transition state



This would also explain the successful competition of the addition reaction with reaction 8.

[17] (a) L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970); (b) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).

[18] In a control experiment, we have qualitatively observed complete dimerization of *N*-benzylideneaniline by sodium naphthalenide in 2 min at −60°. Dimerization has also been effected[14] by the radical anion of diphenyl.

Related reaction conditions have been examined briefly. In DEE, a slower reaction occurred with lithium metal than with sodium to produce **2a**, **2b**, and **3**. In addition, the reaction product always contained unconsumed **1** and also its dimeric reduction product, *N*,*N'*-diphenyl-1,2-bis(*o*-chlorophenyl)ethylenediamine. Thus dimerization of the radical anion of **1** must occur at a rate competitive with its dehalogenation.

With lithium metal and THF, **1** was converted completely into the dimeric diamines **3**; no other products were detected. At the moment, the simplest explanation appears to be that the equilibrium between lithium and **1** (in THF but not in DEE) is considerably more favorable to the radical anion than the corresponding case with sodium. The resulting high concentration of radical anion coupled with the slower rate of addition of the tetrahydrofuryllithium (relative to the sodium analog) permits dimerization of the *N*-benzylideneaniline[10,12,14] to occur as the only detected reaction.[19]

The behavior of the positional isomers of **1** towards alkali metals has also been examined. As already reported,[10] *m*-chlorobenzylideneaniline undergoes normal dimerization. However, the *p*-chloro analog with sodium in THF produced a series of products similar to those from **1** but showed no reaction towards sodium in DEE. The more facile loss of the *o*- and *p*-chloro substituents (relative to the *m*-chloro) undoubtedly reflects the higher charge density found at these positions in the intermediate radical anion. The more rapid elimination of the *o*-chloro substituent relative to the para has also been noted in electrochemical reductions[20] and may reflect a steric effect from the nitrogen anionic center of the intermediate radical anion. This point is being examined further.

In an alternative mechanism Cheng[3] has suggested that the aryl radical produced in reaction 4 could remove the hydrogen atom from the solvent. The resulting solvent radical would be expected to be reduced to the solvent anion. An attempt was made to assess this possibility by conducting the reaction in mixtures of THF and DEE. Should hydrogen removal be effected by radicals then the ratio of solvent containing products would reflect the relative reactivity of the two ethers towards radicals.

In contrast, should anions effect proton removal as shown in eq 6, then the more basic solvent, which would be concentrated near the reaction site by its coordination with the alkali metal counterion, would appear incorporated into the reaction products by a significantly higher factor.

The relative amounts of solvent incorporation into products was assessed by the nmr spectrum of the crude reaction mixture. These results appear in Table II and show that THF reacted four to five times more readily than did DEE. This preferential reaction of THF is more suggestive of proton removal by carbanions[21a,b] than by radicals.[21c]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp melting point apparatus. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer and nmr spectra on a Varian T-60 spectrometer. Chemical shifts are in ppm downfield from internal TMS. Analytical and preparative vapor phase chromatography (vpc) were performed on a Varian-Aerograph 1520 instrument. Mass spectra were determined on a Perkin-Elmer RMU-6E single focusing mass spectrometer operated at 70 eV. Silica gel (0.05–0.2 mm) 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.

All operations with the alkali metal compounds were performed under nitrogen which had been scrubbed by a refluxing solution of benzophenone ketyl in xylene. The solvents (THF and DEE) were purified by distillation from $LiAlH_4$ and stored over and freshly distilled from $LiAlH_4$ immediately before use.

General Procedure.—The preparation and handling of these alkali metal compounds has been described[10] elsewhere. The *N*-(*o*-chlorobenzylidene)aniline (**1**) (2.16 g, 0.01 mol) was dissolved in 75 ± 5 g of solvent and 0.5 g (0.02 g-atom) of freshly cut sodium added. The mixture was shaken 24 hr[22] during which time a precipitate formed and the solution became dark brown. The mixture was drained from the excess metal, cooled to −60°, and quenched by injecting 2.0 ml of methanol.

Product Analysis.—The quenched reaction mixture was diluted with 50 ml of water, and the organic products were isolated by ether extraction. The water layer and washings were diluted to a constant volume, and the ionic chloride was determined gravimetrically (AgCl).

The ether extracts were analyzed by vpc (flame ionization detectors) using a 5 ft × $^1/_8$ in. column packed with 10% Carbowax 20M on 100/120 mesh Chromosorb W at 195° with a He flow rate of 30–40 ml/min. Peaks were identified by "spiking" with authentic samples or by isolation and characterization.

Evaporation of the ether extracts followed by a 24-hr pumping provided the solvent-free reaction mixture. This was analyzed by nmr spectroscopy[23] using the benzylic proton region. These various data are included in Table I for an experiment which titrated as 0.98 g-atom of sodium/mol of initial **1** and showed 59% of the initial chlorine as ionic chloride. Reproducibility of these figures from run to run was ±10%.

In the case of the reactions performed in THF, the benzylic proton region and the α-proton region of the tetrahydrofuryl group overlapped, and an independent nmr analysis was not attempted. By using the vpc analyses and the nmr integrations, an estimate of the content of dimer **3** could be made (see Table I).

Isolation of Reaction Products from DEE Experiments.—Separation of the monomeric products in the reaction mixture was achieved by preparative vpc using a 10 ft × $^3/_8$ in. column packed with 10% Carbowax 20M on 60/80 mesh Chromosorb W operated at 185° (thermal conductivity detector at 220°) with a helium flow rate of 60 ml/min.

The first peak eluting was a nonresolvable mixture of *erythro*- and *threo*-*N*,1-diphenyl-2-ethoxypropylamines (**2a**): ir (max) (KBr) 3440, 2980, 1600, 1500, 1450, 1320, 1090, 1080, 750, 690 cm^{-1}; nmr ($CDCl_3$) δ 0.9–1.3 (m, 6, CH_3), 3.1–3.9 (m, 3, $-CHOCH_2-$), 4.15 (d, 0.67, J = 6 Hz) and 4.47 (d, 0.33, J = 4 Hz) (benzylic H's), 6.4–7.6 (m, 10, aromatic H); m/e (rel intensity) 255 (11, M^+), 210 (2, $M^+ - OEt$), 183 (42), 182 (100, $M^+ - C_4H_9O$), 180 (15), 104 (41), 77 (50).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.95; H, 8.29; N, 5.49. Found: C, 79.85; H, 8.35; N, 5.54.

The second peak, one of the diastereomeric *N*-phenyl-1-(*o*-chlorophenyl)-2-ethoxypropylamines, **2b**, proved to be an oil: ir (max) 3440, 2980, 1600, 1500, 1440, 1310, 1100 (broad), 750, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.02 (t, 3, J = 6 Hz, $-CH_2CH_3$), 1.32 (d, 3, J = 6 Hz, $-CHCH_3$), 2.9–4.0 (m, 3, $-CHOCH_2-$), 4.78 (d, 1, J = 3 Hz, benzylic H), 6.3–7.7 (m, 9, aromatic H); m/e (rel intensity) 291 (2, M^+), 289 (5, M^+), 218 (36, M^+ −

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[19] The possibility that dimerization of the aryl anion formed in reaction 5 might occur with lithium was considered. However, quenching the reaction mixture with D_2O failed to generate ring-deuterated dimers **3**.

[20] (a) T. Kitagama, T. P. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963); (b) W. C. Danen, T. T. Kensler, J. G. Lawless, M. F. Marcus, and M. D. Hawley, *J. Phys. Chem.*, **73**, 4389 (1969).

[21] (a) H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954); (b) H. Gilman and H. A. McNinch, *ibid.*, **27**, 1889 (1962); (c) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

[22] Preliminary experiments showed that at least a 12-hr reaction time was necessary to obtain an "equilibrium uptake" of 1 g-atom of Na/mol of **1** (determined as NaOH).

[23] We are grateful to Dr. L. W. Reeves of this department for providing the well-resolved spectra (determined on an HA-100 spectrometer) which were used in this determination.

TABLE I

COMPOSITION OF THE REACTION PRODUCTS

	S = MeCHOEt			S = 2-tetrahydrofuryl				
	Na		Li	Na		NaNp		Li
	Vpc[a]	Nmr[b]	Vpc[a,c]	Vpc[a]	Vpc + nmr[d]	Vpc[a]	Vpc + nmr	Nmr
PhCH=NPh	2		13	14	11	8	5	...
$\mathrm{Ph\underset{S}{C}HNHPh}$	24	9 12 (30)[e]	Trace	25	19	41	27	...
o-$\mathrm{ClC_6H_4\underset{S}{C}HNHPh}$	25	17 (24)[e]	16	38	29	20	13	...
	49	33 (46)[e]	22	22	17	31	21	...
$\mathrm{(PhCHNHPh)_2}$ racemic		16			24		34	41
meso		12						59

[a] Normalized peak areas. [b] The nmr analysis indicates a 61% conversion of the chlorine into ionic chloride. [c] 49% of o-chlorobenzylideneaniline was also present. Nmr[10] showed that the crude reaction product contained 16% of N,N-diphenyl-1,2-bis(o-chlorophenyl)-ethylenediamine. [d] This combined analysis indicates a 63% conversion of chlorine into ionic chloride (64% was measured). [e] Per cent of total volatile products—for comparison with vpc analysis.

$\mathrm{C_4H_9O}$), 217 (16), 216 (100, $\mathrm{M^+ - C_4H_9O}$), 181 (12), 180 (15), 104 (13), 77 (21).

Anal. Calcd for $\mathrm{C_{17}H_{20}NOCl}$: C, 70.46; H, 6.96; N, 4.83; Cl, 12.23. Found: C, 70.41; H, 6.71; N, 4.66; Cl, 12.00.

The third peak, the second diastereomer of **2b**, was a solid and was recrystallized from diethyl ether: mp 121–123°; ir (max) (KBr) 3400, 2990, 1600, 1510, 1380, 1310, 1250, 1100, 760, 740, 690 cm^{-1}; nmr ($\mathrm{CDCl_3}$) δ 1.03 (d, J = 7 Hz, $\mathrm{-CHCH_3}$) overlapping 1.22 (t, J = 7 Hz, $\mathrm{-CH_2CH_3}$) (total 6 H), 3.62 (q, 2, J = 7 Hz, $\mathrm{-CH_2CH_3}$), 3.8–4.2 (m, 1, $\mathrm{-CHCH_3}$), 5.05 (d, 1, J = 4 Hz, benzylic H), 6.4–7.7 (m, 9, aromatic H); m/e (rel intensity) 291 (2, $\mathrm{M^+}$), 289 (7, $\mathrm{M^+}$), 218 (70, $\mathrm{M^+ - C_4H_9O}$), 217 (43), 216 (100, $\mathrm{M^+ - C_4H_9O}$), 180 (10), 104 (22), 77 (39).

Anal. Found: C, 70.50; H, 7.21; N, 4.91; Cl, 12.05.

This last compound was directly isolated by treating the crude reaction product with a small amount of ether. The crystalline material which separated was recrystallized and proved identical in all aspects with that isolated by preparative vpc.

Treatment of the crude reaction product with warm N,N-dimethylformamide produced, on standing, the crystalline DMF complex[13] of *meso*-**3**. Recrystallization from ethyl acetate–ethanol regenerated *meso*-**3** which was identified by mixture melting point and spectral comparison with authentic material.

Isolation of Reaction Products from THF Experiments.—The reaction products (7.3 g) from 0.03 mol of **1** were chromatographed on 120 g of silica gel using benzene as an eluting agent. Four major fractions were collected. The first, 2.3 g (42%), was *rac*-**3**, mp and mmp with an authentic sample 152–154°.

The second fraction was distilled to give 0.93 g (11%) of a pale yellow viscous oil, bp 167–170° (0.35 mm). Vpc retention times showed it to be a mixture of *erythro*- and *threo*-**4b**. The ir was identical with the authentic reference mixture, and the nmr differed only in the areas of the two benzylic proton doublets. The isolated sample contained 67% of the major isomer while the synthetic sample contained 80%.

The third fraction was distilled, 1.9 g (25%) of a pale yellow oil, bp 155–156° (0.25 mm). This proved to be a mixture of the diastereomeric N-(phenyltetrahydrofurylmethyl)anilines, **4a**, whose ir spectrum was identical with that of the authentic mixture of diastereomeric **4a**. The benzylic proton region of the nmr spectrum showed a larger amount of the crystalline diastereomeric **4a** to be present in this isolated mixture than in the synthesized product, but in other respects the nmr spectrum was identical with that of the reference mixture.

The fourth fraction crystallized, and recrystallization from methanol gave 1.2 g (16%), mp 48–50°, undepressed on mixing with the synthetic crystalline **4a** and having identical ir and nmr spectra.

Reaction in THF–DEE Mixed Solvents.—The procedure was identical with that described earlier, the solvent composition being determined by weighing the reaction vessel after each solvent was distilled in. The isolated mixture of reaction products was pumped under a vacuum of at least 0.1 mm for 24 hr and analyzed by nmr spectroscopy. The ratio of the two solvents incorporated into reaction products was determined by the integrated peak areas of the methyl protons of the DEE-containing products (δ 0.8–1.4) and of the β-tetrahydrofuryl protons of the THF-containing products (δ 1.5–2.0). An additional 24-hr pumping and a second nmr analysis established that the solvent had been completely removed from the reaction products. Table II summarizes these results.

TABLE II

ANALYSIS OF THE MIXED-SOLVENT REACTIONS

Mole ratio, DEE/THF	Mole ratio, 2/4	Relative reactivity, THF/DEE
12.3	2.41	5.1
5.2	1.07	4.9
2.7	0.73	3.7

Reaction of 1 with Sodium Naphthalenide.—Sodium naphthalenide (0.01 or 0.015 mol) was prepared by shaking a mixture of excess sodium, naphthalene, and THF in a Schlenk tube for 24 hr. After draining from excess metal, the solution was cooled to −60° and **1** (0.005 mol) dissolved in THF was injected through a septum into the stirred solution. After 24 hr at room temperature, the mixture was diluted with water and the reactions products isolated by ether extraction. Analyses were conducted as described with the results shown in Table I.

When 0.010 mol of sodium naphthalenide was treated with 0.010 mol of N-benzylideneaniline the reaction product consisted entirely of *meso*- and *rac*-**3**. When the quenching procedure described above was used, the product contained 11% *meso*-**3**. When quenching was performed at −60°, either 2 min or 2 hr after mixing, the product contained 27% *meso*-**3**.

Reference Compounds.—N-**(Phenylfurylmethyl)aniline (5a)** was prepared from 17.1 g (0.1 mol) of N-furfuralaniline[24] and 0.15 mol of phenylmagnesium bromide in diethyl ether. Distillation of the crude product provided 20.0 g (80% yield) of **5a**, bp 154–155° (0.2 mm), which crystallized on standing. Recrystallization from ethanol provided an analytical sample: mp 53–55°; ir (max) 3440, 1600, 1500, 1320, 1020, 750, 700 cm^{-1}; nmr ($\mathrm{CDCl_3}$) δ 4.2 (broad s, 1, NH exchanges with $\mathrm{D_2O}$), 5.6 (s, 1, benzylic H), 6.0–7.5 (m, 13, aromatic and furyl H's).

Anal. Calcd for $\mathrm{C_{17}H_{15}NO}$: C, 81.91; H, 6.07; N, 5.62. Found: C, 81.74; H, 6.12; N, 5.41.

N-**(Phenyltetrahydrofurylmethyl)aniline (4a)** was prepared by hydrogenation of **5a** (5.0 g, 0.02 mol) at 22° in ethanol (120 ml) using 5% rhodium-on-carbon (0.5 g) catalyst[25] and 50 psi of hydrogen pressure for 24 hr. Chromatography of the crude product on 80 g of silica gel with benzene as eluent partially separated the two diastereomers of **4a**. The first fraction eluting was distilled: 2.6 g; bp 155–157° (0.2 mm); ir (max) 3420, 3000, 2900, 1600, 1500, 1320, 1070, 750, 700 cm^{-1}; nmr ($\mathrm{CDCl_3}$) δ 1.6–2.1 (m, 4, tetrahydrofuryl β-H), 3.6–4.5 (m, 4, tetrahydrofuryl α-H and benzylic H), 6.4–7.6 (m, 10, aromatic H); m/e (rel intensity) 253 (8, $\mathrm{M^+}$), 183 (22), 182 (100, $\mathrm{M^+ - C_4H_7O}$), 104 (12), 77 (19).

Anal. Calcd for $\mathrm{C_{17}H_{19}NO}$: C, 80.61; H, 7.56; N, 5.53. Found: C, 80.41; H, 7.58; N, 5.52.

The second fraction which eluted was a solid and recrystallized gave 1.22 g: mp 48.5–49.5°, ir (max) (KBr) 3410, 1600, 1500, 1310, 1060, 1040, 730, 685, 675 cm^{-1}; nmr ($\mathrm{CDCl_3}$) δ 1.4–2.0 (m, 4,

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[24] T. F. West, *J. Soc. Chem. Ind., London*, **61**, 158 (1942).

[25] Hydrogenation with 5% Pd on carbon provided complex reaction mixtures due, in part, to hydrogenolysis.

tetrahydrofuryl β-H), 3.6–4.5 (m, 4, tetrahydrofuryl α-H and benzyl H), 6.4–7.5 (m, 10, aromatic H's); *m/e* (rel intensity) 253 (8, M^+), 183 (31), 182 (100, $M^+ - C_4H_7O$), 104 (21), 77 (33).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.61; H, 7.56; N, 5.53. Found: C, 80.60; H, 7.36; N, 5.50.

The spectral properties of these two diastereomers were very similar. The most obvious difference was in the chemical shift of the benzylic proton doublet. In the solid isomer this was δ 4.41 (J = 5 Hz) while in the "liquid isomer" this was δ 4.20 (J = 5 Hz). This latter material was a mixture of the two isomers as indicated by the nmr spectra (30% solid isomer).

N-(*o*-**Chlorophenylfurylmethyl**)**aniline** (**5b**) was prepared by the addition of 2-furyllithium[26] (0.15 mol) to *N*-(*o*-chlorobenzylideneaniline (21.6 g, 0.1 mol) in *n*-hexane (30 ml). The crude product was distilled to give 26.1 g of viscous oil, bp 155–156° (0.2 mm). The nmr spectrum of this product showed the presence of 10% of the starting material. While the bulk of this product was used in the next step, an analytical sample was isolated by preparative vpc using a 5 ft × 1/4 in. column containing 10% Carbowax 20M on Chromosorb W and operated at 195° with a He flow rate of 50 ml/min: ir (max) 3420, 3060, 1600, 1500, 1320, 1250, 1010, 745, 690 cm^{-1}; nmr ($CDCl_3$) δ 6.04 (s, benzylic H), 6.1–7.6 (m, aromatic and furyl H's).

Anal. Calcd for $C_{17}H_{14}NOCl$: C, 71.95; H, 4.97; N, 4.94; Cl, 12.49. Found: C, 71.97; H, 4.91; N, 4.97; Cl, 12.71.

N-(*o*-**Chlorophenyltetrahydrofurylmethyl**)**aniline** (**4b**) was obtained by hydrogenation of 9.5 g (0.034 mol) of **5b** with 1.0 g of 5% rhodium on carbon in 150 ml of ethanol at 50 psi of hydrogen and 50° for 24 hr. The crude product was chromatographed on 80 g of silica gel with benzene as eluent. The first fraction (5.8 g) was **5b** while the second fraction was distilled to give 2.8 g, bp 175–176° (0.5 mm) of the diastereomeric mixture of **4b**: ir (max) 3400, 1600, 1500, 1310, 1055, 1025, 740, 680 cm^{-1}; nmr ($CDCl_3$) δ 1.5–2.1 (m, 4, β-tetrahydrofuryl H), 3.6–4.5 (m, α-tetrahydrofuryl H), 4.92 (d, 0.2, J = 5 Hz) and 5.07 (d, 0.8, J = 4 Hz) (benzylic H of the two isomers), 6.4–7.6 (m, 9, aromatic H); *m/e* (rel intensity) 289 (2, M^+), 287 (6, M^+), 218 (41, $M^+ - C_4H_7O$), 217 (19), 216 (100, $M^+ - C_4H_7O$), 180 (15), 104 (16), 77 (32), 71 (16).

Anal. Calcd for $C_{17}H_{18}NOCl$: C, 71.11; H, 6.32; N, 4.88; Cl, 12.35. Found: C, 71.15; H, 6.43; N, 4.80; Cl, 12.54.

Registry No.—**1**, 5877-49-6; *erythro*-**2a**, 36736-41-1; *threo*-**2a**, 36736-42-2; *erythro*-**2b**, 36736-43-3; *threo*-**2b**, 36736-44-4; (±)-**3**, 5297-98-3; *meso*-**3**, 6135-06-4, *erythro*-**4a**, 36736-45-5; *threo*-**4a**, 36736-46-6; *erythro*-**4b**, 36736-47-7; *threo*-**4b**, 36736-48-8; **5a**, 36749-19-6; **5b**, 36749-20-9; sodium, 7440-23-5; lithium, 7439-93-2; sodium naphthalenide, 3481-12-7.

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[26] W. E. Truce and E. Wellisch, *J. Amer. Chem. Soc.*, **74**, 5177 (1952). We were unable to effect a successful reaction between *o*-chlorophenylmagnesium bromide and *N*-furfurylideneaniline.

The Diels–Alder Reaction of Polymethylnaphthalenes with Maleic Anhydride

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The effect of polymethyl substitution has been studied in the Diels–Alder reaction with maleic anhydride and eight polymethylnaphthalenes: 1,4-dimethyl- (**1**), 2,3-dimethyl- (**2**), 1,2,3,4-tetramethyl- (**3**), 1,4,5,8-tetramethyl- (**4**), 1,4,6,7-tetramethyl- (**5**), 1,2,3,4,5,8-hexamethyl- (**6**), 1,2,3,4,6,7-hexamethyl- (**7**), and octamethylnaphthalene (**8**). The reaction rates (in chloroform) were in the order of **6** (rel rate 40) > **8** (10) > **7** (3) > **3** (1) > **4** (0.4) > **5** > **2** > **1**. Nmr analysis of the products showed that **1** and **7** gave two structural isomers (1,4 and 5,8 adducts), **2**, **3**, **4**, and **6** gave only 1,4 adducts, and **5** gave the 5,8 adduct exclusively. The endo/exo isomer ratio of the adducts indicated a preferred configuration of the endo isomer (anhydride ring, anti to the benzene nucleus) for the naphthalenes bearing methyl groups on the reacting position while the exo isomer was preferred for the naphthalenes bearing no methyl group on that position. Examination of the reversibility of the reaction showed that the endo isomer is kinetically preferred while the exo isomer is thermodynamically more stable. A structural preference rule is discussed.

The Diels–Alder reaction of naphthalene with benzynes, acetylene dicarboxylates, and maleic anhydride exhibits only limited yields.[1] However, naphthalenes with alkyl substituents show enhanced reactivity towards dienophiles.[2] When methyl groups are in peri positions or even vicinal to each other, they may be shifted from their normal positions to out-of-plane positions and may complicate the diene system. This assumption is supported by X-ray analysis of octamethylnaphthalene by Donaldson and Robertson,[3] who mention that the methyl groups in this molecule are significantly displaced from the plane of the ring, but they gave little comment concerning the distortion of the naphthalene nucleus. Similarly, Gafner and Herbstein[4] have suggested a double-bladed propeller structure for octachloronaphthalenes. The possibility exists that the naphthalene nucleus itself loses its coplanarity, and the diminution of a planar geometry, if any, will change the electronic structure of the nucleus and may be reflected in the dienoid character of the ring halves.

In relation to the chemistry of octamethylnaphthalene,[1,5] we examined the Diels–Alder reaction of maleic anhydride with symmetrically substituted polymethylnaphthalenes with the purpose of obtaining further information on the effect of multialkyl substitution, especially in peri positions. In the present study it has been found that the reacting position in the naphthalene nucleus is influenced by varying positions of methyl substitution regardless of the number of methyl groups on the reacting ring, and that the endo/exo isomer distribution in the products depends on the position of methyl substituents as well. The peri interaction was also evidenced not only by the rate enhancement but in the high yields of thermally stable adducts for highly substituted polymethylnaphthalenes.

(1) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. III, Part B, Elsevier, Amsterdam, 1956, p 1361.

(2) M. C. Kloetzel, R. P. Dayton, and H. L. Herzog, *J. Amer. Chem. Soc.*, **72**, 273 (1950); M. C. Kloetzel and H. L. Herzog, *ibid.*, **72**, 1991 (1950).

(3) D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953).

(4) G. Gafner and F. H. Herbstein, *Nature* (*London*), **200**, 130 (1963).

(5) H. Hart and A. Oku, *J. Chem. Soc. D*, 254 (1972).