(*p*-bromophenacyl ester) 82° (lit.[16a] 85°)] and acetone [mp (2,4-dinitrophenylhydrazone) 124–125° (lit.[16b] 126°)].

In a reaction of 3.3 g (0.028 mol) of pinacol with 4.87 g (0.018 mol) of potassium peroxydisulfate and 0.042 g (0.00025 mol) of silver nitrate, 2.18 g (0.018 mol) of pinacol was recovered unreacted and 1.05 g (0.018 mol, 90% of theory) of acetone was formed as determined by gas chromatographic analysis of the reaction mixture.

Reaction of 0.88 g (0.010 mol) of pyruvic acid with 4.32 g (0.016 mol) of potassium peroxydisulfate and 0.042 g (0.00025 mol) of silver nitrate yielded 0.59 g (0.0098 mol, 98% of theory) of acetic acid as determined by gas chromatographic analysis of the reaction mixture. Carbon dioxide was evolved during the course of this reaction but not measured quantitatively.

Registry No.—**1**, 76-09-5; **2**, 115-22-0; **3**, 127-17-3; peroxydisulfate ion, 15092-81-6; allyl acetate, 594-87-7; Ag$^{(I)}$, 14701-21-4.

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(16) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1956: (a) p 311; (b) p 362.

The Reductive Dimerization of Schiff Bases by Alkali Metals. Isomerization of the Dimeric Dianions

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The alkali metal induced reductive dimerization of substituted *N*-benzalanilines (ArCH=NPh) in ether solvents is examined. Particular attention is directed toward the isomerization of the diastereomeric mixture of dimeric dianions which are the primary products of the reaction. By means of cross-product experiments, it is shown that the isomerization results from an equilibrium between the dimeric dianions and the monomeric radical anion of the original *N*-benzalaniline. The observed effects of solvent and substituent groups correlate well with this conclusion.

The synthetic value of the reductive dimerization of carbonyl compounds or their derivatives is reflected in the variety of reagents which have been developed to effect this reaction.[1-10] A characteristic feature of the reaction is the formation of diastereomeric mixtures and this feature has stimulated efforts to elucidate the factors controlling the diastereomeric ratio.[11] Among the many examples of reductive dimerization, the reaction of *N*-benzalaniline with alkali or alkaline earth metals in anhydrous solvents has the intriguing feature that essentially only one diastereomer is formed, *dl-N,N'*,1,2-tetraphenylethylenediamine, under selected reaction conditions.[12,13] As has been shown,[12] the preponderance of the *dl* isomer arises from an isomerization of the diastereomeric dimeric dianions initially formed in the reductive dimerization, an isomerization which predominates in the *dl* dianion.

It was the intention of the present investigation to distinguish between the two mechanisms previously suggested[12] for the isomerization (see Scheme I). The first mechanism (path a, dissociative mechanism) depends on an equilibrium between the radical anion **2** and the dimeric dianions **3** to allow the kinetic product to isomerize to the thermodynamic one. The second mechanism (path b, carbanionic mechanism) relies on the abstraction of a benzylic proton by the basic amine anion **3**, forming a carbanion **4** which can then epimerize.

Should a mixture of two *structurally* different dimeric dianions **3** be present in solution, then the anionic mechanism would predict that the equilibrium mixture should consist essentially of the two *dl*-dimeric dianions. On the other hand, the dissociative mechanism would predict the formation of these and a cross dimer formed by the coupling of the two different radical anions present.

Such an experiment required two different diamines **5** whose anions were known to isomerize during formation and whose nmr spectra were sufficiently different that the reaction mixture could be analyzed. To optimize the formation of cross products, the *meso* isomer was preferred. In addition, a process was needed to convert the diamine to its corresponding dianion in order to induce isomerization.

With this purpose in mind, a number of substituted benzalanilines **1** were subjected to reductive dimerization with sodium in tetrahydrofuran (THF) or diethyl ether (DEE). The data pertaining to isomerization is summarized in Table I. Authentic samples of the dimeric diamines were isolated either from these reaction mixtures or from similar mixtures generated with aluminum amalgam. Table II summarizes the physical properties of the diamines and Table III the product composition from the aluminum amalgam reductions which, unlike the alkali metal reductions, contain large amounts of monomeric reduction products.

The stereochemistry of the dimeric diamines **5** is assigned on the assumption that the resonances of the benzylic protons in the *meso* isomer appear downfield from those of the *dl* isomer.[14,15] Such an assumption

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(1) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 50–77.

(2) R. Adams and E. W. Adams, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1941, p 459, and references cited therein.

(3) M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961).

(4) W. E. Bachman, *J. Amer. Chem. Soc.*, **53**, 2672 (1931).

(5) H. Thies, H. Schoenenberger, and K. H. Bauer, *Arch. Pharm. (Weinheim)*, **291**, 620 (1958).

(6) O. Anselmino, *Ber.*, **41**, 623 (1908).

(7) W. Stuhmer and G. Messwarb, *Arch. Pharm. (Weinheim)*, **286**, 221 (1953).

(8) W. Schlenk, J. Apprenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914).

(9) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 281 (1928).

(10) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970.

(11) J. H. Stocker, R. M. Jenevein, and D. H. Kern, *J. Org. Chem.*, **34**, 2810 (1969).

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

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

(14) J. Wiemann, G. Dana, S. Thuan, and M. Brami, *C. R. Acad. Sci., Ser. C*, **258**, 3724 (1964).

(15) P. Beak and C. R. Payet, *J. Org. Chem.*, **35**, 3281 (1970).

SCHEME I

POSSIBLE MECHANISMS FOR THE ISOMERIZATION

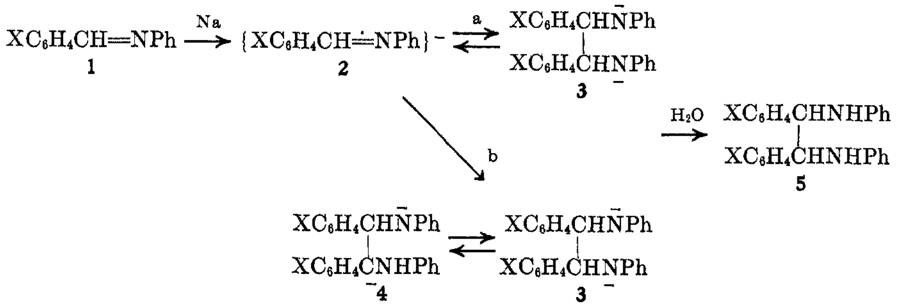
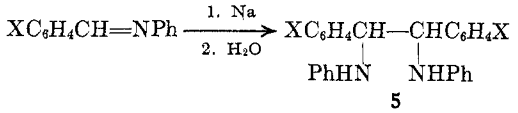


TABLE I

PRODUCT COMPOSITION FROM THE REACTION



$$XC_6H_4CH{=}NPh \xrightarrow[2.\ H_2O]{1.\ Na} \underset{PhHN}{XC_6H_4CH}{-}\underset{NHPh}{CHC_6H_4X}$$

5

X	% *dl*-**5**[a] in THF: Initial[b]	Final[c]	$t_{1/2}$,[d] hr	% *dl*-**5**[a] in DEE: Initial[b]	Final[c]	$t_{1/2}$,[d] hr
H	67	93	4.5	64	68	
o-Me	70	92	>1	43	85	13
m-Me	69	100	2.5	66	66	
p-Me	73	81	35[e]	59	59	
o-MeO	78	100	2		78	*f*
m-MeO	60	90	3	50	60	>50[e]
p-MeO	65	69		52	56	
m-Cl	100	100	>1	55	72	25

[a] Per cent of dimeric diamine; no significant amounts of the *N*-benzylaniline were detected. [b] At 0.5-hr reaction time. [c] At 24-hr reaction time. At longer reaction times, the *N*-benzylaniline began to appear. [d] *Time for the product composition to* reach a value halfway between the initial and equilibrium compositions. [e] Estimated assuming 90% *dl* at equilibrium. [f] Only 12% reacted in 24 hr.

is consistent with the stereochemistry of the one dimer of known stereochemistry,[7] is consistent with the melting points of the compounds, and is consistent with the observed isomerizations in which the isomer with the downfield proton isomerizes to the one with the upfield (*meso* → *dl*).

Conversion of the diamines to their corresponding dianions was successfully accomplished by treating them with the required amount of the disodium stilbene complex. This method[16] was selected in preference to phenylsodium or sodium hydride[17] since it utilized homogeneous solutions, and the reaction conditions were identical with the dimerization process itself. Control experiments with *N*,*N*′,1,2-tetraphenylethylenediamine (**5**, X = H) showed that the equilibrium composition was achieved on reacting either the *meso* or the *dl* isomer under these conditions.

For the cross-product experiment, the two dimeric diamines selected were **5** (X = H) and **5** (X = *o*-CH_3) since isomerization was observed in both cases and the chemical shifts of the benzylic protons of the *meso* and *dl* isomers of either compound were different. Anticipating the formation of a cross product, the expected reaction mixture was generated by reductively dimerizing a mixture of the two Schiff bases **1**, X = H and X = *o*-Me. The cross product, 1-(*o*-methylphenyl)-*N*,*N*′,2-triphenylethylenediamine (**6**), was easily observed in the nmr spectrum, the methyl resonance being clearly separated from the others and the benzylic protons appearing as an AB quartet. The isolation of this product was accomplished as well.

A mixture of *meso*-**5** (X = H) and *meso*-**5** (X = *o*-Me) when treated with an equivalent amount of disodium–stilbene complex produced the same reaction mixture as generated from the mixture of two Schiff bases. The mixed dimer **6** similarly treated formed the same reaction mixture. And, finally, in the simplest experiment of all, two *separate* reductive dimerizations using **1** (X = H) and **1** (X = *o*-Me) were carried to completion and the dimeric dianions so formed were mixed. Again, the isolated diamine mixture contained the cross product.

These three experiments establish that a dissociative mechanism is responsible for the isomerization observed in the reductive dimerization of Schiff bases by sodium metal. Since the dimeric dianions are themselves formed by the coupling of radical anions, the principal of microscopic reversibility[18] would dictate that dissociation of the dimeric dianions to radical anions (*i.e.*, path a, Scheme I) is occurring.[19] Szwarc[20a–c] has examined a related equilibrium involving the radical anion and dimeric dianion of 1,1-diphenylethylene. Two dissociation mechanisms were postulated. In the terminology used by Szwarc these equilibria are

$$^-DD^- \rightleftharpoons 2D^-$$

$$^-DD^- + D \rightleftharpoons D^- + {}^-DD\cdot \rightleftharpoons D + 2D^-$$

where D is the monomer, D^- the radical anion, and $^-DD^-$ the dimeric dianion.

Either of these equilibria (or both) would explain the observations recorded here. In addition, these equilibria coupled with the rapid electron transfer between radical anion and unsaturated monomer[20d,e] would predict that a Schiff base such as **1** (X = H) added to an equilibrating dianion such as **3** (X = *o*-Me) will result in the formation of mixed dimer **6**.

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(16) The obvious choice of butyllithium was eliminated by the fact that the lithium salts of tetraphenylethylenediamine shows no isomerization (see ref 12).

(17) In control experiments with NaH, considerable amounts of *N*-benzylaniline were formed from tetraphenylethylenediamine (see also ref 12).

(18) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 250.

(19) Attempts to observe an esr signal from these equilibrating systems were unsuccessful. We wish to thank Dr. T. Gough of this department for his assistance in these experiments. A similar failure has been reported by L. I. Petersen, *J. Amer. Chem. Soc.*, **89**, 2677 (1967).

(20) (a) S. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962); (b) M. Szwarc and R. Asami, *J. Amer. Chem. Soc.*, **84**, 2269 (1962); (c) M. Matsuda, J. Jagur-Grodzinski, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **288**, 212 (1965); (d) J. Jagur-Grodzinski and M. Szwarc, *ibid.*, **288**, 224 (1965); (e) E. R. Zabolotny and J. F. Garst, *J. Amer. Chem. Soc.*, **86**, 1645 (1964).

TABLE II

PROPERTIES OF DIMERIC DIAMINES **5**

				δ, ppm		Found, %			
X		Registry no.	Mp, °C	Benzylic	X	C	H	N	Cl
o-Me	*meso*	32979-86-5	139–141	5.16	1.97	85.57	7.30	7.23[a]	
	dl	32979-87-6	132–133	4.80	1.88	85.74	7.17	7.12	
m-Me	*meso*	32979-88-7	90–93	4.88	2.20	85.67	7.23	7.27	
	dl	32979-89-8	140–141	4.50	2.27	85.68	7.10	7.06	
p-Me	*meso*	27549-75-3	138.5–141	4.90	2.28	86.23	7.00	7.06	
	dl[b]	27549-69-5	131–131.5	4.55	2.27				
o-MeO	*dl*[c]	33021-00-0	168–170	5.03	3.63	79.49	6.69	6.66[d]	
m-MeO	*meso*	32979-92-3	122–123	4.95	3.62	79.10	6.52	6.60	
	dl	32979-93-4	110–112	4.53	3.63	79.34	6.66	6.69	
p-MeO	*meso*	32979-94-5	186–188	4.87	3.73	79.38	6.86	6.51	
	dl	32979-95-6	143–144	4.52	3.73	79.37	6.86	6.49	
o-Cl	*meso*	32979-96-7	172–174	5.53		72.35	5.07	6.40	16.33[e]
	dl	32979-97-8	140–142	5.24		72.12	5.24	6.42	16.39
m-Cl	*meso*	32979-98-9	136–139	4.91		71.83	5.11	6.36	16.53
	dl	32979-99-0	128–129	4.47		72.25	5.05	6.44	16.45
p-Cl	*meso*[f]	32980-00-0	198–199	4.94					
	dl[g]	32980-01-1	137	4.25					

[a] Theory: C, 85.88; H, 7.19; N, 7.14. [b] Reported mp 130°: H. Thies, H. Schonenberger, and K. H. Bauer, *Arch. Pharm.* (*Weinheim*), **291**, 620 (1958). [c] The *meso* isomer not isolated. [d] Theory: C, 79.21; H, 6.65; N, 6.60. [e] Theory: C, 72.06; H, 5.12; N, 6.47; Cl, 16.36. [f] Reported mp 194–195 (H. Thies, *et al.*, footnote *b*) and 195–196°: J. Huet, *Bull. Soc. Chim. Fr.*, 973 (1964). [g] Reported mp 136° (J. Huet, footnote *f*).

TABLE III

PRODUCT COMPOSITION FROM THE ALUMINUM AMALGAM REDUCTION OF SCHIFF BASES

	Product composition, %[a]		
$XC_6H_4CH{=}NPh$, X	*meso*-**5**	*dl*-**5**	Monomer (δ)[b]
o-Me	33	38	29 (4.19)
m-Me	34	44	22 (4.12)
o-MeO	0	55	45 (4.31)
m-MeO	28	35	37 (4.21)
o-Cl	33	67	0 (4.30)
m-Cl	38	38	24 (4.25)
p-Cl	15	45	40 (4.04)

[a] Analyzed by nmr. [b] $XC_6H_4CH_2NHPh$ (chemical shift of benzylic proton).

This has been observed both with the dimeric dianion generated by reductive dimerization and by treatment of the diamine with disodium–stilbene.

Since any of these dissociations involves the radical ion (*e.g.*, path a, Scheme I), those factors which stabilize the radical anion would be expected to promote isomerization. Thus isomerization is more prevalent in THF, with its greater solvating power, than in DEE. In a relevant experiment, the addition of 10% hexamethylphosphoramide to THF effected isomerization in the reductive dimerization of **1** (X = *p*-MeO).

Substituents also modify the stability of the radical anion. Electron-donating substituents would be expected to destabilize the radical anion and indeed isomerization is inhibited by *p*-OCH_3 or *p*-CH_3. Electron-withdrawing groups, assisting the delocalization of electrons, should facilitate isomerization and a *m*-Cl substituent[21] does so. However, ortho substituents promote isomerization. Presumably this is due to the increased steric bulk[22] of the *o*-tolyl groups which assists the dissociation of the dimeric dianion to the radical anion.

Experimental Section[23]

Starting Materials.—The *N*-benzalanilines **1** were prepared from the freshly distilled substituted benzaldehyde and aniline according to a published procedure.[24] The properties of the Schiff bases produced agreed with the reported values. The solvents used for the reduction, after purification by distillation from lithium aluminum hydride, were stored over this reagent and distilled into the reaction vessel when needed. The reaction mixtures were analyzed by the procedure previously described.[12,13]

General Procedure for the Reductive Dimerization.—A modified Schlenk tube[25] was flushed with nitrogen, the Schiff base added (0.01 mol), and the solvent distilled in (75 ± 5 g). The tube was sealed and transferred to a drybox and the sodium metal (0.02 g-atom) was cut and added. After resealing and removing from the drybox, the mixture was shaken on a horizontal shaker. Reaction began almost at once as evidenced by streams of color flowing from the surface of the metal.

Aliquot samples of the solution were removed at 0.5, 1, 2, 4, 8, and 24 hr and quenched in water and the liberated sodium hydroxide was titrated with standard acid. With one exception, (**1**, X = *o*-MeO in DEE) all Schiff bases were completely converted to dimer (1 g-atom of Na per mole of Schiff base) in 2–4 hr. The titrated samples were then extracted with ether and the organic material was isolated and analyzed for its dimeric composition. These data are summarized in Table I.

Isolation of 1,2-Diaryl-*N*,*N*′-diphenylethylenediamines.—The *dl* isomers were isolated by recrystallization of those mixtures which isomerized. In one instance (**5**, X = *p*-MeO) isomerization was promoted by using tetrahydrofuran containing 10% hexamethylphosphoramide, the final composition being *dl*, 86.4%, and *meso*, 13.6%.

The *meso* isomers were obtained by crystallizing the DMF complex from solution.[26] This procedure operated most efficiently when the *meso*/*dl* ratio was no smaller than 0.5. Consequently, the alkali metal promoted reductions were often unsatisfactorily as sources of the *meso* isomers. With aluminum amalgam as a reducing agent, the products were protonated as rapidly as they formed and isomerization was avoided. This

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(21) The *o*- and *p*-chloro analogs behave in a markedly different manner under these reaction conditions This behavior will be described in a later communication.

(22) W. Theilacker and M.-L. Wessel-Ewald, *Justus Liebigs Ann. Chem.*, **594**, 214 (1955).

(23) Melting points are uncorrected and were determined with a Mel-Temp apparatus in open capillaries. The nmr spectra were recorded on a Varian T-60 nmr spectrometer. The nitrogen used was Matheson purified grade further purified by passing through a benzophenone ketyl solution in refluxing xylene. Analyses are by M-H-W Laboratories, Garden City, Mich.

(24) L. A. Bigelow and H. Eatough, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1941, p 80.

(25) J. W. B. Reesor, J. G. Smith, and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

(26) (a) R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956); (b) R. Jaunin and P. Courbat, *ibid.*, **43**, 2029 (1960).

proved to be a convenient source of material from which the *meso* isomers could be isolated. The physical properties of the isolated dimers are summarized in Table II and the composition of the reduction products formed in the aluminum amalgam reductions are shown in Table III.

Preparation of the Cross Dimer, 1-(*o*-Methylphenyl)-*N*,*N*′-,2-triphenylethylenediamine (**6**).—A solution containing 1.81 g (0.01 mol) of **1** (X = H) and 1.95 g (0.01 mol) of **1** (X = *o*-Me) in 200 ml of THF was treated with 0.92 g (0.04 g-atom) of sodium and shaken for 24 hr. The orange solution was drained from the excess sodium, treated with methanol, diluted with water, and extracted with ether. After removal of the solvent, the residue was analyzed by nmr by using the methyl resonances to determine the relative amounts of cross dimer **6**, *dl* "homo dimer" **5** (X = o-Me), and the small amount of monomeric reduction product *N*-(*o*-methylphenyl)aniline. The contribution made by **5** (X = *o*-Me) and **6** to the area of the benzylic resonances was then calculated and subtracted from the total area to give the amount of *dl*-**5** (X = H) (see Table IV).

TABLE IV

FORMATION OF THE CROSS DIMER

	Product anal, %				
		Homo dimers			
Reaction conditions[a]	Cross dimer **6**	*dl*-**5** (X = *o*-Me)	*dl*-**5** (X = H)	*meso*-**5** (X = H)	Monomer[b]
Mixed Schiff bases, **1** (X = H and *o*-Me)	51	19	27	<1	3
Mixed dimeric dianions, **3** (X = H and *o*-Me)	51	19	25	<1	5
Mixed diamines, *meso*-**5** (X = H) and *meso*-**5** (X = *o*-Me) + DSS[c]	54	18	22	<1	6
Cross dimer **6** + DSS[c]	47	17	34	2	<1
Dianion **3** (X = *o*-Me) treated with 2 equiv of **1** (X = H)	22	15	19	<1	5[d]
meso-**5** (X = H) + DSS,[c] then treated with 1 equiv of **1** (X = *o*-Me)	27	10	40	<1	*e*

[a] 24-hr reaction time. [b] *N*-(*o*-Methylphenyl)aniline. [c] Disodium-stilbene. [d] Product contained 21% of **1** (X = H) and 19% of **1** (X = *o*-Me). [e] Product contained 13% of **1** (X = H) and 10% of **1** (X = *o*-Me).

Isolation of the cross dimer **6** was effected by recrystallization from methanol to remove the more soluble *dl*-**5** (X = *o*-Me). The solid so obtained was recrystallized from DMF when the DMF complex of *dl*-**5** (X = H) separated. The filtrate from this was acidified with 6 *N* HCl and the white precipitate was filtered, washed with water, dried, and recrystallized from absolute ethanol to give **6**: mp 125–128°; nmr ($CDCl_3$, D_2O washed) δ 6.4–7.3 (m, 19 aromatic H), 4.81 (d, 1 H, CHCH, *J* = 8.0 cps), 4.54 (d, 1 H, CHCH, *J* = 8.0 cps), 2.03 (s, 3 H, CH_3).

Anal. Calcd for $C_{27}H_{26}N_2$: C, 85.67; H, 6.93; N, 7.40. Found: C, 85.68; H, 7.05; N, 7.32.

In an alternative procedure, each Schiff base in THF was treated with sodium in separate Schlenk tubes. After a 24-hr reaction time, the solutions were drained from the excess metal into the same nitrogen-filled flask and stirred for a further 24 hr. The isolated product was analyzed as described with the result shown in Table IV.

A similar cross product was prepared from **1** (X = H) and **1** (X = *m*-Me) and isolated by recrystallization from methanol: mp 120–121.5°; nmr ($CDCl_3$, D_2O washed) δ 6.4–7.4 (m, 19 aromatic H), 4.53 (broad s, 2 benzylic H), 2.33 (s, 3 H, CH_3).

Anal. Calcd for $C_{27}H_{26}N_2$: C, 85.67; H, 6.93; N, 7.40. Found: C, 85.89; H, 6.90; N, 7.58.

Isomerization with the Disodium–Stilbene Complex.—A solution of 0.005 mol of the selected diamine in 25 ml of THF was treated at room temperature under N_2 with a solution (THF) of 0.005 mol of the disodium–stilbene complex.[25] The color changed from the deep red of the stilbene complex to orange within 10–15 min. The solution was stirred 24 hr and quenched by the addition of methanol, and the product was isolated by diluting with water and extracting with ether.

Both *meso*- and *dl*-*N*,*N*′,1,2-tetraphenylethylenediamine (**5**, X = H) so treated produced the equilibrium composition of 93% *dl* and 7% *meso*.

A mixture of 0.911 g (0.0025 mol) of *meso*-**5** (X = H) and 0.981 g (0.0025 mol) of *meso*-**5** (X = *o*-Me) was isomerized under these conditions (see Table IV). Similarly treated was a solution of 1.41 g (0.004 mol) of the cross dimer, 1-(*o*-methylphenyl)-*N*,*N*′-2-triphenylethylenediamine, in 25 ml of THF. Product composition is shown in Table IV.

Registry No.—**6**, 33021-01-1.

Acknowledgment.—The authors wish to acknowledge helpful discussions with Dr. D. Mackay of this department. This research was financially supported by the National Research Council of Canada.

Reactivity Differences in Competitive Metal Hydride Reductions of α,β-Unsaturated and Saturated Ketones

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Competitive reduction experiments involving mixtures of saturated and α,β-unsaturated six-membered ring ketones and lithium aluminum hydride or lithium tri-*tert*-butoxyaluminohydride have shown a large reactivity difference between the two types of ketones. Both hindered and unhindered ketone systems were employed as substrates. The unsaturated ketones were consistently less reactive than the saturated ketones. This reactivity difference is enhanced with the more selective tri-*tert*-butoxyaluminohydride reagent.

Competition experiments in which α,β-unsaturated and saturated six-membered ring ketones are made to compete for limited amounts of lithium aluminum hydride ($LiAlH_4$) or lithium tri-*tert*-butoxyaluminohydride (LTAH) reveal remarkable reactivity differences between the two types of ketones. The experiments described involve the inverse addition of standardized[1] solutions of $LiAlH_4$ in ether, or weighed amounts of LTAH in tetrahydrofuran (or ether), to stirred mixtures of two ketones. These experiments were the outgrowth of observations of the low reactivity of several cyclic enones toward $LiAlH_4$ reductions. The reactions carried out, together with the major products obtained, are listed in eq 1–3.

Analyses of the products were carried out by gas chromatography directly on the concentrated reaction products and also after catalytic hydrogenation with palladium on charcoal (except for the isophorone–dihydroisophorone competitive reduction, eq 1). Catalytic

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[1] H. Felkin, *Bull. Soc. Chim. Fr.*, 347 (1950).