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Titanium(III) Chloride Mediated Reduction of 1-Nitro-2-phenylethenes

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The reaction of 1-nitro-2-phenylethenes (β-nitrostyrenes) with aqueous titanium(III) chloride afforded substituted pyrroles in addition to the expected reduction products, oximes and carbonyl compounds. 2-Substituted 1-nitro-2-phenylethenes yielded divinylamine derivatives instead of pyrroles. The reaction mechanism has been rationalized by taking account of the electron transfer from titanium(III) species to the nitro olefins, followed by protonation, dimerization, cyclization, and/or hydrolysis.

Much attention has been paid to the role of conjugated nitroalkenes as versatile intermediates in organic synthesis, since they may be transformed into legions with diverse functionalities.1,2) The conversion of nitroalkenes to alkylamines has been accomplished through the use of catalytic hydrogenation, lithium aluminum hydride, or sodium borohydride–boron trifluoride.3) Carbonyl compounds and their oximes have been prepared from nitroalkenes by means of titanium(III) chloride,4) Raney nickel/sodium phosphinate,5) chromium(II) chloride,6) lithium trialkylhydroborate,7) zinc/acetic acid,8) lead/acetic acid,9) sodium stannite,10) tin(II) chloride,11,12) and electrochemical means.13,14) In addition, nitriles are synthesized by reactions of nitroalkenes with iodotrimethylsilane15) or by a cathodic reduction in the presence of titanium(IV) chloride.16)

We previously reported that the reaction of 1-nitro-2-phenylethenes **1** with titanium(III) chloride yields divinylamine derivatives **4** and pyrroles **5**, in addition to the expected oximes **2** and carbonyl compounds **3**.17) This paper is concerned with the synthetic utility and the mechanistic features of the titanium(III) chloride-mediated reduction of several 1-nitro-2-phenylethenes (**1**, substituted β-nitrostyrenes).

Results and Discussion

A report by McMurry and Melton4) indicates that 1-nitrocyclooctene is readily reduced with aqueous titanium(III) chloride in tetrahydrofuran at pH <1 to give cyclooctanone in 55% yield. However, we found that the reaction of **1a**—**d** with titanium(III) chloride under almost neutral conditions (pH=6.5, an ammonium acetate buffer) results in dimerized and/or cyclized products in addition to the expected carbonyl compounds or oximes. The product distribution was dependent on the structural features of the starting 1-nitro-2-phenylethenes (Table 1). The reaction of **1a** with titanium(III) chloride (6 mole equiv) afforded a small amount of 3,4-diphenylpyrrole (**5a**) along with 1,4-dinitro-2,3-diphenylbutane (**6a**). The formation of **5** and **6** is the first example of the reductive dimerization of nitro olefins by chemical means. Since **6a** was thought to be a possible intermediate for pyrrole forma-

Table 1. Reaction of 1-Nitro-2-phenylethenes with Titanium(III) Chloride[a,b]

Nitroethene	Conditions	Products and yields/%[c]				
		2	**3**	**4**	**5**	Others
1a	0 °C/0.5 h	—	—	—	3	**6a**: 7
	35 °C/24 h[d]	—	—	—	32	
1b	0 °C/0.5 h	—	35	—	6	**7b**: 7
	35 °C/24 h[d]	—	60	—	32	
1c	35 °C/24 h[d]	—	61	—	31	
1d	0 °C/1.5 h	62	6	—	—	
	35 °C/24 h[d]	—	38	—	20	
1e	0 °C/5 h	55	10	—	—	
1f	0 °C/4 h	46	15	32	—	
	30 °C/0.5 h[d]	19	22	50	—	
1g	0 °C/20 h	56	27	—	—	
	35 °C/24 h[d]	—	84	14	—	
1h	0 °C/6 h[d]					**8**: 33; **9**: 15
	35 °C/14 h[e]					**8**: 43; **9**: 13
1i	0 °C/0.2 h[f] (pH 7)					Benzil dioxime: 54
1j	0 °C/1.5 h (pH 7)					Benzophenone: 56

a) Taken in part from Ref. 17. b) In aqueous tetrahydrofuran at pH 6.5. Molar $TiCl_3$/**1** ratio was 6. c) Isolated yields. d) Molar $TiCl_3$/**1** ratio was 12. e) Molar $TiCl_3$/**1** ratio was 18. f) In acetonitrile.

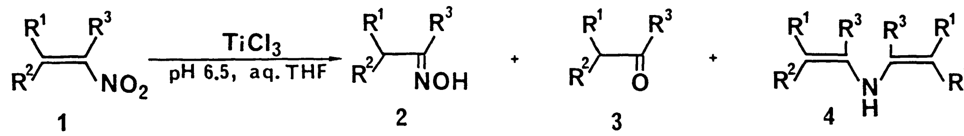
tion, the reaction was conducted with 12-fold molar titanium(III) chloride at an elevated temperature. Expectedly, **5a** was obtained in an improved yield (32%). The reaction conditions were then examined to improve the yields of **5a**. As shown in Table 2, the reaction with 12 molar titanium(III) chloride in neutral aqueous 1,4-dioxane at 35 °C gave **5a** in a satisfactory yield (50%). Phenylacetaldehyde (**3a**) could not be isolated because of its instability under the reaction conditions employed.[18] Similar results were obtained for a series of substituted 1-nitro-2-phenylethenes (**1b**—**d**) possessing a hydrogen atom at the β-position to the nitro group (R^2=H). In all cases, pyrroles **5b**—**d** as well as carbonyl compounds **3b**—**d** were obtained. Although many procedures have been documented for pyrrole synthesis,[19] the present reaction may be taken as a new entry into symmetrically substituted pyrroles. The major advantages of the present method are that the operation is simple and the starting compounds are easily prepared from the corresponding aldehydes and nitroalkanes.

Table 2. Reduction of **1a** with Aqueous Titanium(III) Chloride under Various Conditions[a)]

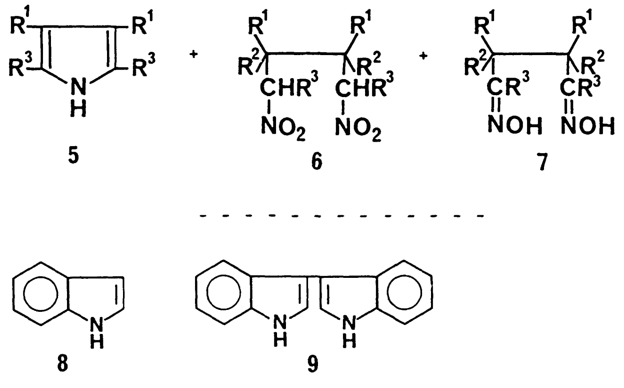
Solvent	$TiCl_3$ (molar equivalent)	Yield of **5a**/%[b)]
Tetrahydrofuran	6	18
	12	32
Methanol	6	25
	12	43
Acetonitrile	6	22
	12	35
1,4-Dioxane	6	32
	12	50
	12[c)]	28
	12 (pH=4.4)	23
	12 (pH<1)	0

a) At 35 °C for 24 h, pH=6.5. b) Isolated yields. c) At 65 °C.

The reaction of **1a** with an insufficient amount (3 mole equiv) of titanium(III) chloride yielded **6a** (15%), **7a** (3%), and 2,3-diphenyl-4-nitrobutanal oxime (**11**, 23%). These partially reduced products were supposed to be the intermediates leading to pyrrole **5a**. Accordingly, **6a** was synthesized by the Michael reaction of **1a** with 1-nitro-2-phenylethane, and the product was separated to the *meso*- and *dl*-**6a**. Titanium(III) chloride reduction of these two isomers did not afford **5a** at all; however, the disodium salt of **6a** could be reduced under the present reduction conditions to produce **5a**. Thus, the dinitronate anion (**B**) of **6a** should be the actual intermediate, and the formation of pyrroles is rationalized by taking account of the stepwise electron transfer-protonation process (Scheme 2).[4] Electron transfer from the titanium(III) species to **1** gives rise to an anion radical (**A**) stabilized by the 2-phenyl substituent. This anion radical is further reduced to give an oxime **2**, which is readily reduced by aqueous titanium(III) chloride to give an imine (overall six-electron transfer).[20,21] Upon hydrolysis this imine gives rise to a carbonyl compound **3**. The formation of a carbonyl compound by direct hydrolysis of oxime is unlikely under the present conditions. The anion radical (**A**) would dimerize to give an intermediate (**B**) which is further reduced by titanium(III) chloride to a diimine through the dioxime **7**. Elimination of ammonia from the imine–enamine tautomeric form (**C**) of the diimine intermediate finally affords the pyrrole derivative **5**. In the reductions of 1-nitro-1-alkenes by known methods,[4–14] no dimeric products were reported. The formation of the dimeric products is therefore characteristic of the reaction with titanium(III) chloride. Chelation of two anion radical intermediates with titanium(III or IV) species would hold both radical centers sufficiently close



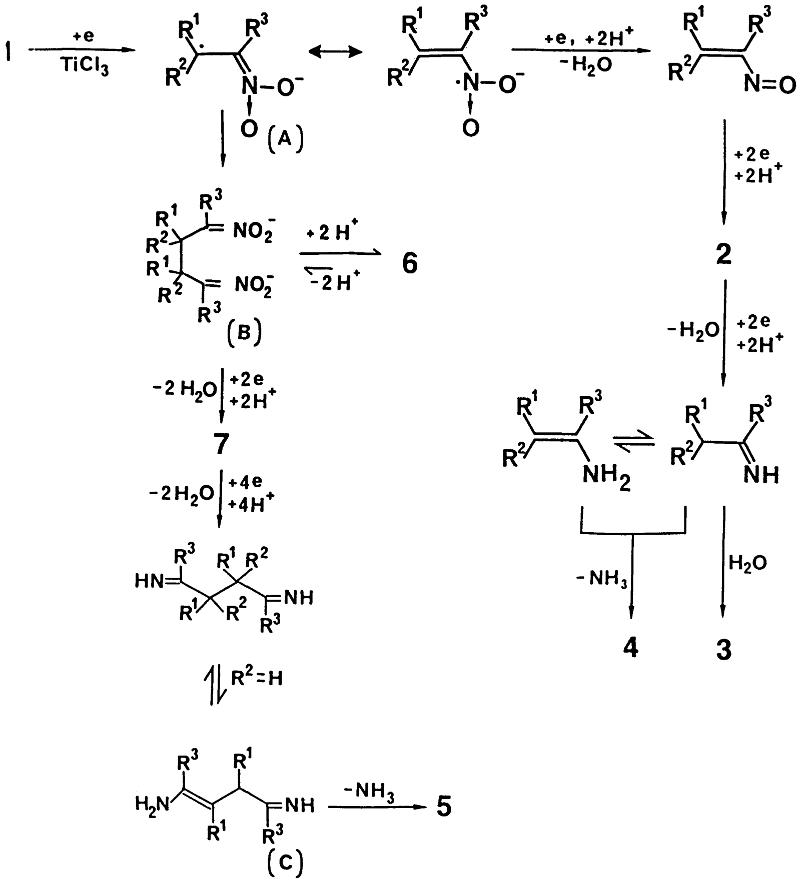
	R^1	R^2	R^3
1a:	Ph	H	H
b:	Ph	H	Me
c:	Ph	H	Et
d:	Ph	H	Ph
e:	H	Ph	Ph
f:	Ph	Ph	H
g:	Ph	Ph	Me
h:	o-$NO_2C_6H_4$	H	H
i:	Ph	NO_2	Ph
j:	Ph	Ph	NO_2



Scheme 1.

to achieve radical coupling, just as was proposed for the electrochemical hydrodimerization of cinnamate esters.[22)]

On the other hand, the reaction of nitroolefins possessing no β-hydrogen atom **1f,g** with titanium(III) chloride yielded divinylamine derivatives **4f,g**. In these cases carbonyl compounds **3f,g** and oximes **2f,g** were produced, but no pyrrole was detected. The yield of **4f** increased at the expense of that of **2f** with excess titanium(III) chloride at higher temperature. The divinylamines **4f,g** may be regarded as forms of cross-conjugated dienamines (an open chain version of pyrrole). Many cross-conjugated dienamines have been described in the literature.[23)] However, those dienamines which possess a structural feature of C=C–N–C=C, like **4f,g**, have been only little documented,[24,25)] although many of those possessing the C=C–C=C–N and $\mathrm{C{=}\underset{\displaystyle N}{\underset{|}{C}}{-}C{=}C}$ functionalities have been synthesized and their characteristics are thoroughly elucidated.[23)] The mechanism of divinylamine formation can be considered to be as follows. The intermediate radical anions (**A**) from **1f,g** are highly stabilized and have no tendency to dimerize to (**B**), due to the presence of two bulky phenyl groups on the radical center. The electron transfer-protonation process thus gives rise to oximes **2f,g**, which are reduced further to give imine intermediates. These imines yield carbonyl compounds by hydrolysis or tautomerize to enamines. Spectroscopic studies[24,26)] have shown that the equilibrium is usually almost completely in favor of the imine form for simple nonconjugated aldimines and ketimines. Nevertheless, imine–enamine tautomerism has been clearly demonstrated for reactions in which the enamine tautomer reacts with a variety of electrophiles.[27)] In the present case the primary enamines are stabilized by conjugation with the two phenyl groups. Intervention of the imine–enamine tautomerism was further confirmed by trapping these species. In the presence of aniline, the titanium(III) chloride reduction of **1f** yielded *N*-(2,2-diphenylethylidene)aniline, produced by the addition of aniline to an imine (2,2-diphenylethanimine) followed by elimination of ammonia. On the other hand, addition of *N*-benzylidene butylamine afforded *N*-benzylidene-2,2-diphenylvinylamine, produced by the addition of an enamine (2,2-diphenylvinylamine) to the Schiff base followed by the elimination of butylamine. From these observations, it is clear that the nucleophilic addition of the enamine to the imine followed by the elimination of ammonia afforded divinylamine **4f**[28)] as the final product. The product selectivity is thus governed by both the nature and number of substituents at C2 of the starting 1-



Scheme 2.

nitroethenes.

As expected, 1-nitro-2-(2-nitrophenyl)ethene (**1h**) yielded indole (**8**). 3,3′-Bi-1*H*-indole (**9**) was also produced by dimerization of the intermediate radical anion (**A**) followed by cyclization. The absence of 3,4-bis(2-aminophenyl)pyrrole, another possible cyclization product from the dimerized intermediate, indicates a predominance of the imine tautomer in the imine–enamine tautomerism of the dimerized intermediate. The titanium(III) chloride reduction of 1,2-dinitro-1,2-diphenylethene (**1i**) and 1,1-dinitro-2,2-diphenylethene (**1j**) resulted only in the formation of benzil dioxime and benzophenone (hydrolysis product), respectively.

Experimental

All melting points were determined on a micro hot-plate melting-point apparatus and are not corrected. IR spectra were measured on a JASCO IRA-3 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-90Q and PS-100 spectrometers. Chemical shifts are given in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on an ESCO EMD-05A spectrometer.

Substituted nitroethenes were prepared according to methods described in the literatures.[29] Solvents were purified as usual. Aqueous titanium(III) chloride solution was purchased from Wako Chemical Ind., and titrated before use.

General Procedure of Titanium(III) Chloride Reduction. A buffered titanium(III) chloride solution was prepared by adding ammonium acetate (5.5 g, 71 mmol) in 25 ml of water to a 1.76 M aqueous titanium(III) chloride solution (11 ml) under nitrogen (1 M=1 mol dm^{-3}). Adjustment of the pH was achieved by adding 10% (w/v) aqueous ammonia to the solution. A solution of 1-nitro-2-phenylethene (**1**, 3 mmol) in 14 ml of tetrahydrofuran was rapidly added to the buffered titanium (III) chloride solution; the solution was stirred at 0 °C under nitrogen. The reaction was monitored by TLC. After the substrate was completely consumed, the reaction mixture was extracted several times with diethyl ether. The combined extracts were washed successively with aqueous sodium hydrogencarbonate and sodium chloride solutions, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography. The results are given in the Tables.

Representative Products of the Titanium(III) Chloride Reduction. 3,4-Diphenylpyrrole (5a):[30] Oil, IR (neat) 3400, 1720, 1600, and 1560 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=6.7 (2H, d, *J*=2.6 Hz), 7.1 (10H, m), and 8.0 (1H, br); MS *m*/*z* 219 (M$^+$), 218, 190, 188, and 164.

1,4-Dinitro-2,3-diphenylbutane (6a): A *meso*-*dl* mixture; mp 178—180 °C; IR (KBr) 1550 and 1380 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=3.5—5.2 (6H, m) and 7.3 (10H, m); MS *m*/*z* 300 (M$^+$), 254, 223, 208, and 194. Found: C, 63.79; H, 5.50%. Calcd for C$_{16}$H$_{16}$N$_2$O$_4$: C, 63.99; K, 5.37%.

meso and *dl*-**6a**[31] were prepared.

meso-**6a**: Mp 101—102 °C; IR (KBr) 1554, 1380, 790, and 696 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=3.7—4.1 (2H, br. t), 4.8—5.3 (4H, br), and 6.8—7.4 (10H, s); ^{13}C NMR (CDCl$_3$) δ=45.7, 77.3, 128.6, 128.7, 129.1, and 134.3; MS *m*/*z* 300 (M$^+$), 254, 223, 208, and 194. Found: C, 63.85; H, 5.30; N, 9.25%. Calcd for C$_{16}$H$_{16}$N$_2$O$_4$: C, 63.99; H, 5.37; N, 9.33%.

dl-**6a**: Mp 240—243 °C; IR (KBr) 1554, 1382, 790, and 700 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=3.7—3.9 (2H, br. t), 4.1—4.3 (2H, br. dd), 4.7—5.1 (2H, br. t), and 7.2—7.7 (10H, m); ^{13}C NMR (DMSO-*d*$_6$) δ=46.8, 78.7, 127.9, 128.0, 128.8, and 137.5; MS *m*/*z* 300 (M$^+$), 254, 223, 208, and 194.

2,5-Dimethyl-3,4-diphenylpyrrole (5b):[32] Mp 145—148 °C; IR (KBr) 3350, 1600, 1500, 1450, and 770 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2 (6H, s), 7.0 (10H, m), and 7.3 (1H, br); MS *m*/*z* 247 (M$^+$), 246, 202, 179, and 77.

3,4-Diphenyl-2,5-hexanedione Dioxime (7b):[32] Mp 370 °C (decomp); IR (KBr) 3240 and 1500 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=1.5 (6H, s), 4.2 (2H, s), 7.2 (10H, m), and 9.7 (2H, s); MS *m*/*z* 296 (M$^+$), 279, 262, 247, and 188.

2,5-Diethyl-3,4-diphenylpyrrole (5c):[33] Mp 149—150 °C; ^{1}H NMR (CDCl$_3$) δ=1.2 (6H, t), 2.6 (4H, q), 7.1 (10H, m), and 7.5 (1H, br); MS *m*/*z* 275 (M$^+$), 274, 260, 246, 231, and 230.

Benzyl Phenyl Ketone Oxime (2d):[34] Mp 86—89 °C; IR (KBr) 3200, 1605, 1495, and 1450 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.1 (2H, s), 6.5—7.7 (10H, m), and 9.3 (1H, br); MS *m*/*z* 211 (M$^+$), 193, 164, 119, 103, and 91.

2,3,4,5-Tetraphenylpyrrole (5d):[35] Mp 213.5—214 °C; ^{1}H NMR (CDCl$_3$) δ=6.8—7.4 (20H, m) and 8.2 (1H, br); MS *m*/*z* 371 (M$^+$), 370, 293, 265, and 216.

Diphenylacetaldehyde Oxime (2f):[36] Mp 117—118.5 °C; IR (KBr) 3260, 1600, 1450, 1250, 960, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.9 (1H, d, *J*=7 Hz), 7.1—7.5 (10 H, s), 7.8 (1H, d, *J*=7 Hz), and 8.0 (1H, s); ^{13}C NMR (CDCl$_3$) δ=51.3, 127.2, 128.6, 128.8, 140.3, and 153.1; MS *m*/*z* 211 (M$^+$), 194, 180, 167, and 115.

Bis(2,2-diphenylvinyl)amine (4f):[24] Pale yellow needles (benzen-hexane), mp 143.5—144.5 °C; IR (KBr) 3360 and 3200 cm^{-1}; UV (MeCN) $\lambda_{\max}$ 360 nm ($\varepsilon_{\max}$=25600); ^{1}H NMR (CDCl$_3$) δ=6.6 (2H, s) and 7.0 (20H, m, Ph and NH); ^{13}C NMR (CDCl$_3$), geminal two phenyl rings are not equivalent, δ=117.5 (Ph$_2\underline{\text{C}}$=), 126.7, 127.3, 128.2, 129.4 (C=$\underline{\text{C}}$HN-), 129.7, 130.3, 131.2, 139.4, and 142.6; MS *m*/*z* 373 (M$^+$), 372, 296, 206, and 179. Found: C, 89.86, H, 6.28, N, 3.77%. Calcd for C$_{28}$H$_{23}$N: C, 90.04, H, 6.21, N, 3.75%.

1,1-Diphenyl-2-propanone Oxime (2g):[37] Mp 160—162 °C; IR (KBr) 3420, 1605, 1495, and 1455 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.8 (3H, s), 4.9 (1H, s), 7.1 (10H, m), and 8.5 (1H, s); MS *m*/*z* 225 (M$^+$), 208, 193, 167, 165, and 152. Found: C, 80.03, H, 6.83%. Calcd for C$_{15}$H$_{15}$NO: C, 79.97, H, 6.71%.

Bis(1-methyl-2,2-diphenylvinyl)amine (4g): Oil, IR (CHCl$_3$) 3400 and 1610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2 (6H, s), and 6.8—7.7 (21H, m, Ph and NH); MS *m*/*z* 207 (M$^+$−Ph$_2$C=CHMe), 206, 178, 165, and 130.

3,3′-Bi-1*H*-indole (9):[38] Mp 280 °C (decomp); IR (KBr) 3380 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=6.7—7.8 (10H, m) and 10.9 (2H, br); MS *m*/*z* 232 (M$^+$), 231, and 203.

Reduction of 1a with 3 Molar Equivalents of Titanium(III) Chloride. Reaction of **1a** (4.47 g, 30 mmol) with 90 mmol of titanium(III) chloride under the standard conditions for 45 h yielded, after usual work-up, **6a** (15%), **7a** (3%), and 2,3-diphenyl-4-nitrobutanal oxime (**11**, 23%).

2,3-Diphenyl-4-nitrobutanal Oxime (11): An isomer mixture; mp 205—210 °C; IR (KBr) 3400, 1555, 1460, 1385, and 705 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=3.5—5.0 (8H, m), 6.8 (1H, d, *J*=8 Hz), 7.2 (1H, d, *J*=8 Hz), 7,1—7.7 (20H, m), 10.3 (1H, s), and 10.7 (1H, s); ^{13}C NMR (acetone-*d*$_6$) δ=44.5 and 49.2, 49.5 and 50.8, 80.3, 128.6 and 129.6, 129.0 and 128.0, 129.8 and 129.7, 129.8 and 129.9, 130.2 and 130.4, 130.2 and 130.5, 139.5, 140.5, 151.1 and 151.4; MS *m*/*z* 284 (M$^+$), 283, 253, 207, and 205. Found: C, 67.34; H, 5.95; N, 9.78%. Calcd for

$C_{16}H_{16}N_2O_3$: C, 67.51; H, 5.67; N, 9.85%.

Reduction of Disodium Salt of 6a with Titanium(III) Chloride. A solution of disodium salt (173 mg, 0.5 mmol) of **6a** in methanol (8 ml) was added to a buffered solution (pH=6.5) of titanium(III) chloride; the mixture was stirred for 24 h at room temperature. After the usual work-up, 20 mg (18%) of **5a** was obtained.

Titanium(III) Chloride Reduction of 1f in the Presence of Aniline or *N*-Benzylidenebutylamine. 1,1-Diphenyl-2-nitroethene (**1f**, 3 mmol) was reduced in a buffered aqueous tetrahydrofuran solution (pH 6.5) containing titanium(III) chloride (18 mmol) and aniline (3 mmol) at 30 °C for 2 h. After the usual work-up, the product was chromatographed on silica gel to give *N*-(2,2-diphenylethylidene)aniline (62%). This compound was easily oxidized by air to give benzophenone (57%) and *N*-formylaniline (47%). A similar reaction carried out in the presence of *N*-benzylidenebutylamine (15 mmol) yielded *N*-benzylidene-2,2-diphenylvinylamine (40%) as yellow crystals: Mp 131.5—133.5 °C; IR (KBr) 1620, 1590, 1550, 1480, and 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.0—7.7 (16H, m, Ph×3 and C=C$\underline{H}$-N) and 8.3 (1H, s, -N=C$\underline{H}$Ph); MS m/z 283 (M$^+$), 206, 178, and 165. Found: C, 89.20; H, 6.21; N, 4.89%. Calcd for $C_{21}H_{17}N$: C, 89.05, H, 6.01; N, 4.95%.

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