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METAL-ASSISTED REACTIONS—PART 11[1]

RAPID REDUCTION OF N-NITROSOAMINES TO N,N-DISUBSTITUTED HYDRAZINES; THE UTILITY OF SOME LOW-VALENT TITANIUM REAGENTS

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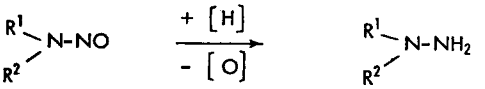
Abstract—The rapid reduction of N-nitrosoamines to N,N-disubstituted hydrazines by a low-valent titanium reagent is described. The reagent is selective in that many other functional groups are unaffected by it. The nature of the low-valent titanium reagent is discussed in terms of experimental results of comparisons of its reactivity and that of other low-valent titanium reducing agents.

The reduction of N-nitrosoamines to N,N-disubstituted hydrazines (equation 1) is a valuable reaction because of the widespread use of hydrazines as drugs, pesticides, fungicides, herbicides, antioxidants, and rocket propellants and the ease of preparation of N-nitrosoamines. There are several methods for effecting this reduction based on dissolving metals,[2] electrolysis,[3] hydride reagents,[4] and catalytic reduction with molecular hydrogen.[5] None of these methods appears to be broadly applicable to all N-nitrosoamines and often the reductions described apply only to a narrow range of closely similar compounds. A major difficulty in effecting the reduction lies in the ease with which both the N-nitrosoamine and the resulting hydrazine are cleaved across the N–N bond to give the parent amine.



(1)

Following our earlier work on catalytic transfer reduction of various functional groups,[6] we attempted to use this method to effect the reaction shown in equation 1. Despite trials with a variety of hydrogen-donors (cyclohexene, formic acid and formates, phosphinic acid and phosphinates, and hydrazine) with various heterogeneous catalysts based on Pd, Pt, Rh, and Ru, it was not possible to isolate hydrazines. In all attempted reductions, the initially produced hydrazine was reduced rapidly at the N–N bond to give an amine and ammonia. The failure of these catalytic experiments led us to investigate the use of low-valent titanium reagents as these have been reported to effect "deoxygenation" of some functional groups. For example, epoxides can be deoxygenated to alkenes,[7] ketones and aldehydes can be deoxygenatively coupled to form alkenes,[8] and sulphoxides can be reduced to sulphides.[9] Although no hydrogen is required for these reductions, we surmised that N-nitrosoamines might be reduced by low-valent titanium to "nitrenoid" compounds bound chemically to the titanium and that these "nitrenoids" would yield the hydrazine on hydrolysis with acid or alkali. The easy cleavage of the N–N bound might be avoided because no hydrazine should be formed until the final hydrolysis step.

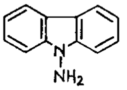
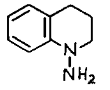
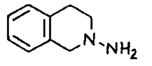
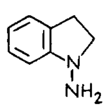
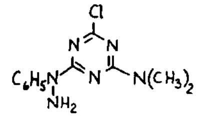
A Ti(II) reagent prepared by reaction of $TiCl_4$ with magnesium in a mixture of diethyl ether and methylene chloride was found to convert N-nitrosoamines into N,N-disubstituted hydrazines in good to excellent yields. A range of typical reductions and yields is shown in Table 1. One N-nitroamine was reduced also to the corresponding hydrazine (Table 1).

The low-valent titanium reagent is nominally a Ti(II) species and is formally similar to one used to effect nitrogen fixation;[10] the latter also effected the reduction shown in equation 1. Other Ti(0) and Ti(II) reagents were found to be ineffective or inefficient for producing hydrazines. A comparative discussion on these reagents, based on experimental results, follows.

Low-valent titatium reagents

Titanium combines directly with many elements and, in its Ti(0) and Ti(II) states, is a powerful electron donor.[11] The preparation of simple Ti(II) compounds has been made difficult by the ease with which such compounds can dissociate to the Ti(0) and Ti(III) states.[11,12] However, $TiCl_2$ appears to have been prepared[12b,13] and π-dicyclopentadienyltitanium is widely used.[14] The relative instability of the Ti(II) state and the readiness of titanium to combine with other elements leads to considerable ambiguity concerning the actual composition and nature of many previously described low-valent titanium reagents. The reagent prepared by reduction of $TiCl_4$ with one molar proportion of Zn, which has been used to deoxygenate sulphoxides,[9] was found to reduce N-nitrosoamines to N,N-disubstituted hydrazines. However, because the Zn reacted sluggishly with the $TiCl_4$, powered Mg was used instead. Thus, reduction of $TiCl_4$ with magnesium in CH_2Cl_2/Et_2O quickly produced a formal Ti(II) reagent (A) which was equally effective for the reduction (1). Reduction of $TiCl_4$ with magnesium in tetrohydrofuran (THF) is reported to lead to a complex nitride, $NTiMg_2Cl_2$. THF, in which elemental nitrogen has been fixed.[10] This reagent (B) is nominally similar to reagent (A) used for the work described here so we also

Table 1. Reduction of N-nitrosoamines to N,N-disubstituted hydrazines by low-valent titanium

Hydrazine	Yield(%)[a]	Derivative[b]	Tlc Separation[c]
$(C_6H_5)_2NNH_2$	96	A,B	V (0.57,0.43)
	92	B	W (0.71,0.51)
$(cyclo\text{-}C_6H_{11})_2NNH_2$	47[d]	C	X(0.56,0.79)
$C_6H_5(CH_3)NNH_2$	90	B	
$[(CH_3)_2CHCH_2]_2NNH_2$	95	C	Y(0.54,0.13)
	100	B	Y(0.69,0.22)
	84	B	W(0.55,0.26)
	62	B	Z(0.71,0.34)
	11[e]		Z(0.72,0.30)

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[a] Purity and yield checked by tlc, gc and NMR.

[b] The hydrazines were identified as monoacetyl (A), benzylidene (B) and/or oxalate (C) derivatives (see experimental for references).

[c] The solvent systems were: V($CHCl_3$), W($CHCl_3/Me_2CO$, 9 : 1 v/v), X(cyclohexane/EtOH, 9 : 1 v/v), Y(CH_2Cl_2/Et_2O, 95 : 5 v/v), Z(Et_2O). Rf values are shown in parentheses for first, N-nitrosoamine and second, hydrazine.

[d] This yield is based on the yield of isolated derivative (C). Tlc and NMR revealed little evidence for impurities in the crude hydrazine.

[e] Prepared from the corresponding nitroamine, supplied by Shell Research Ltd. The low yield may have been caused by the low solubility of the starting material and the products in the solvents used.

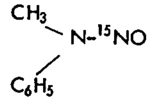
investigated the effectiveness of (B) for the reduction of N-nitrosoamines. No indication is given in the reported preparation of reagent (B)[10] concerning the length of time needed for complete absorption of nitrogen.

As prepared by us, the reagent absorbed only a quarter of the expected nitrogen after two hours and a half after 7 hr. Thus, absorption of nitrogen is rather slow for reagent (B). If used immediately after preparation, reagent (B) reduces N-Nitrosoamines to hydrazines as does reagent (A). However, if reagent (B) is allowed to absorb nitrogen, its ability to reduce N-nitrosoamines to hydrazines decreases proportionately to the amount of N_2 absorbed. Reagent (B) prepared under argon was equally effective for the reduction. Reagent (A) did not absorb nitrogen and it appears likely that the two reagents (A, B) are not similar despite both being able to effect the reduction of N-nitrosoamines and despite both being nominal Ti(II) species.

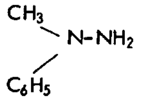
A third type of low-valent titanium species (reagent C) can be made by reduction of $TiCl_4$ or $TiCl_3$ with $LiAlH_4$. The nature of this reagent is unknown but nominal Ti(0) or Ti(II) states are prepared by adjusting the molar ratio of $TiCl_4$ (or $TiCl_3$) to $LiAlH_4$ and these reagents have been used to effect deoxygenation of epoxides to alkenes[15] and to de-oxidatively couple aldehydes and ketones to form alkenes.[16] This reagent (C; Ti(0) or Ti(II)) did not reduce N-nitrosoamines to hydrazines (1) but it did cleave the N–N bond to yield the parent amine. Because of the ambiguity concerning the nature of this reagent (C)[17] and some reports that it was ineffective,[17] an alternative low-valent titanium species (reagent D) has been prepared by reduction of $TiCl_3$ with potassium;[18] this reagent is probably finely-divided Ti(0) and is effective for the deoxidative reactions described above.[15,16] We have prepared similarly nominal Ti(0) and Ti(II) states by reduction of $TiCl_4$ with a sodium/potassium alloy. This alloy was chosen because it is liquid at room temperature[19] and reacts with $TiCl_4$ at a lower temperature than does Na or K alone. A simple, convenient method for preparation of this useful alloy is described in the experimental section. When $TiCl_4$ was reduced with two molar proportions of the Na/K alloy, the resulting mixture (reagent D; a mixture of $NaCl/KCl/TiCl_2$ or possibly Na_2/K_2TiCl_4[20]) with N-nitrosodiphenylamine mostly cleaved the N–N bond to give the parent amine but did give some N,N-diphenylhydrazine. When the molar proportion of Na/K alloy to $TiCl_4$ was increased to 4 : 1 (reagent E; probably mostly Ti(0) metal), attempted reduction of N-nitrosodiphenylamine gave only diphenylamine. This result with Ti(0) together with the observation that Ti(0) from $TiCl_4$ and $LiAlH_4$ (reagent C) also did not give hydrazines led us to reduce $TiCl_4$ with two molar equivalents of Mg rather than the one molar equivalent used to prepare the Ti(II) reagent(A). This new reagent (F), which was nominally Ti(0), like the other Ti(0) reagents did not reduce N-nitrosodiphenylamine to N,N-diphenylhydrazine but gave back mostly the N-nitrosoamine together with some diphenylamine.

Thus, reagents (A) and (B) were best for conversion of N-nitrosoamines to hydrazines (1) with (A) being preferred because it did not appear to absorb elemental nitrogen. The other low-valent titanium reagents either had little effect on the nitrosoamine or cleaved the N–N bond to yield the parent amine. Although $TiCl_3$ has been reported to reduce aromatic nitro compounds to amines[21] and aliphatic nitro compounds to imines,[22] it had no effect on the nitrosoamines examined in our work.

The reduction (1) with reagent (A) was fast (5–30 min at room temperature) and this speed of reduction contrasts sharply with the conditions recommended for "deoxygenation" reactions with other low-valent titanium reagents. For example, deoxygenation of epoxides to olefins requires 3 h,[15] deoxygenation of phenols (*via* phosphate esters) requires 6–16 h,[23] and "deoxidative" coupling of ketones or aldehydes requires 16 h,[16] (all at 65°). Therefore, it appeared possible that reagent (A) could be selective in its reduction of N-nitrosoamines in the presence of other functional groups. This supposition was mostly realised, as shown by the unreactivity of benzyl chloride with reagent (A) but there were unexpected exceptions. First, benzaldehyde with reagent (A) was reduced partly to benzyl alcohol but mostly to 1,2-diphenylethane-1,2-diol; this reductive coupling was much faster than that reported[24] for reagents (C, D). Second, the oxiran ring of decene-1 epoxide was opened rapidly to give a mixture of 1-chloro-2-hydroxydecane and 2-chloro-1-hydroxydecane; in contrast to the reported deoxygenation of epoxides,[15] this epoxide was not deoxygenated with reagent (A).



(I)



(II)

Apart from the slow absorption of nitrogen by reagent (B), it has been observed that reduction of π-dicyclopentadienyltitanium dichloride with Mg in the presence of o-fluorochlorobenzene under N_2 yielded aniline and ammonia after hydrolysis[25] i.e. atmospheric N_2 had been incorporated into the organic substrate. Although in our experiments with reagent (A) no absorption of N_2 with the reagent alone had been found, it was possible that some of the nitrogen in the NH_2 part of the N,N-disubstituted hydrazines formed in the reaction shown in equation 1 could have arisen from atmospheric nitrogen. Accordingly, N-[^{15}N]-nitroso-N-methylaniline (I) was prepared from ^{15}N-labelled $NaNO_2$ 99.95% isotopic purity. The isotopic purity of the nitrosoamine(I) was checked by mass spectrometry. After reduction with reagent (A), under N_2, mass spectrometric examination of the isolated 1-methyl-1-phenylhydrazine(II) showed that the ^{15}N-label had been retained completely and no ^{14}N-isotope was present in the NH_2 group. Therefore, reduction of N-nitrosoamines with reagent (A) proceeds without cleavage of the N–N bond during the formation of the hydrazine.

Conclusion

Of several low-valent titanium reagents investigated as possible reductants for N-nitrosoamines to hydrazines only one (reagent A) was found to be generally useful. Other Ti(0) and Ti(II) reagents either cleaved the N–N bond of the nitrosoamine to give amine or were ineffective. Some observations on the nature of the low-valent titanium reagents have been made and a convenient method for the preparation of Na/K alloys, liquid at room temperature, is described.

EXPERIMENTAL

The N-nitrosoamines and N,N-disubstituted hydrazines are mostly known compounds but, because much of the data are old or derivatives have not been described, brief analytical details are included here. The ^{1}H-nmr spectra of the N-nitrosoamines showed clear evidence for restricted rotation about the N–N bond[26] in $CDCl_3$ at the temperature of measurement (30–32°); the ratios of rotational isomers are approximately as shown.

N–Nitrosoamines ($R^1R^2N.NO$). $R^1 = R^2 = C_6H_5$, m.68–71(EtOH; lit.[27] 66–67°), δ 6.9–7.3 (m,2H), 7.3–7.6(m, 8H); R^1R^2N = carbazolyl, m.77–79° (EtOH; lit.[28] 82.5°), δ 7.2–7.65 (m, 4H), 7.65–8.0(m, 2H), 8.0–8.3 and 8.3–8.7 (multiplets, each 1H, ratio of rotational isomers, 1 : 1); $R^1 = R^2$ = cyclo-C_6H_{11}, m.107–109° (60–80° petroleum ether/acetone, 3 : 1; lit.[29] 104–105°), δ 0.9–2.2(m, 20H), 3.4–4.0 and 4.6–5.14 (multiplets, each 1H, ratio of rotational isomers, 1 : 1); $R^1 = CH_3, R^2 = C_6H_5$, b.p. 135–137°/13mm, m.14–16°(lit.[30] b.p. 135–137°/13mm, m.14.7°), δ 3.42(s, 3H), 7.48 (sharp m, 5H); $R^1 = R^2 = (CH_3)_2CHCH_2$ b.p. 62–66°/0.2–0.3mm (lit.[31] b.p. 213–218°), δ 1.0 (two d, 12H), 1.5–2.4 (m, 2H), 3.45 and 4.0 (doublets, each 1H, ratio of rotational isomers, 1 : 1); R^1R^2N = 1,2,3,4-tetrahydroquinolinyl, m. ~ 20° (lit.[32] "yellow oil"), δ 1.7–2.5(m, 2H), 2.75(t, 2H), 3.85(t, 2H), 7.1–7.45(m, 3H), 7.85–8.2(m, 1H); R^1R^1N = 1, 2, 3, 4-tetrahydroisoquinolinyl, m.48–50° (60–80° petroleum ether; lit.[33] 53°), δ 3.3–3.85(m, 2H), 3.87 and 4.55 (each a triplet, total 2H, ratio of rotational isomers, 1 : 3), 4.85 and 5.40 (each a singlet, total 2H, ratio of rotational isomers, 1 : 3) R^1R^2N = 1-indolinyl, m.86°(EtOH; lit.[34] 83°), δ 3.0–3.45(t, 2H), 4.0–4.4(t, 2H), 7.15–7.55(m, 3H), 7.75–8.05(m, 1H).

Hydrazines ($R^1R^2N.NH_2$). $R^1 = R^2 = C_6H_5$, m.34.5–36° (40–60° petroleum ether; lit.[35] 34.5°); acetyl derivative, m.184–186°(lit.[36] 186°); benzylidene derivative, m.125–126° (EtOH; Found: C, 83.7; H, 6.0; N, 10.5%. $C_{19}H_{16}N_2$ req. C, 83.8; H, 5.9; N, 10.3%); R^1R^2N = carbazolyl, m.150–152°(EtOH; lit.[28] 147°), δ 4.35(broad s, 2H; exchange with D_2O), 7.35(m, 6H), 8.05(d, 2H); benzylidene derivative, m.142–144°(EtOH; Found: C, 84.3; H, 5.4; N, 10.5. $C_{19}H_{14}N_2$ req. C, 84.4; H, 5.2; N, 10.4%); $R^1 = R^2$ = cyclo-C_6H_{11}, m.168–170°d (EtOH; lit.[37] 162°); $R^1 = CH_3$, $R^2 = C_6H_5$, b.p. 58–60°/0.035mm (lit.[38] 106–109°/13mm) δ 2.9(s, 3H), 7.05(m, 6, H), 4.4(broad s, 2H; exchange with D_2O); benzylidene derivative, m.106–108°(EtOH; lit.[38] 106–107°; Found: C, 79.8; H, 6.5; N, 13.5 Calc. for $C_{14}H_{14}N_2$; C, 80.0; H, 6.7; N, 13.3%); dibenzoyl derivative, m.166–167° (Found: C, 76.2; H, 5.7; N, 8.7. $C_{21}H_{18}O_2$ req. C, 76.3; H, 5.5; N. 8.5%); $R^1 = R^2 = (CH_3)_2CHCH_2$[38], δ 2.05 (m, 2H), 2.2(d, 4H) 2.8(s, 2H; exchange with D_2O); oxalate, m. 163°d (EtOH/H_2O; Found: C, 51.3; H, 10.0; N, 12.5. $C_{10}H_{22}N_2O_4$ req. C, 51.3; H, 9.4; N, 12.0%); R^1R^2N = 1,2,3,4-tetrahydroquinolinyl, m.54–55° (EtOH;[39] 55°), δ 2.07(m, 2H), 2.75(t, 2H), 3.28(t, 2H), 3.58(S, 2H), 6.3–7.3(m, 4H); benzylidene derivative, m.79–80°(EtOH; Found: C, 81.3; H, 6.8; N, 11.7. $C_{16}H_{16}N_2$ req. C, 81.3; H, 6.8; N, 11.9%); R^1R^2N = 1,2,3,4-tetrahydroisoquinolinyl,[40] δ 3.0(s, 4H), 3.20(s, 2H; exchange with D_2O), 3.85(s, 2H), 7.2(s, 4H); benzylidene derivative, m.67–68°(EtOH; Found: C, 81.0; H, 7.3; N, 11.3. $C_{16}H_{16}N_2$ req. C, 81.3; H, 6.8; N, 11.9%); R^1R^2N = 1-indolinyl lit.[15] m.5–6°); benzylidene derivative, m.140–141° (EtOH; Found: C, 80.9; H, 6.3; N, 12.4 $C_{15}H_{14}N_2$ requires C, 81.1; H, 6.4; N, 12.6%)

Preparation of titanium reagent (A) for reduction of N-nitrosoamines. To a mixture of CH_2Cl_2 and Et_2O (250 ml; 4 : 1 v/v), was added $TiCl_4$(6.6 ml; 0.06 mole) slowly with stirring to give a yellow complex. Magnesium powder (1.5g; 0.06 mole) was added to this mixture under N_2 or Ar without cooling and stirring was continued for 2.5 hr at room temperature to give a brownish-black solution. This solution was used immediately for reduction of N-nitrosoamines.

Typical reduction of N-nitrosoamine to the corresponding hydrazine. To a solution of the Ti(II) reagent (A) prepared as above was added an ethereal solution of N-nitrosodiphenylamine (3.0 g; 0.015 mole) at room temperature with stirring. After 30 min, dil HCl (H_2O/conc HCl, 40 : 1 v/v) was added and stirring continued for 1 hr. The resulting purple solution was made alkaline by addition of NaOH and extracted with Et_2O to give N,N-diphenylhydrazine (2, 5g; 95% yield). Tlc on SiO_2 in $CHCl_3$ showed that no starting material remained and only a slight trace of diphenylamine was observed. Addition of benzaldehyde (1.5g) in EtOH (5 ml) to the crude product gave the benzylidene derivative, (3.25g; 81% yield) m.p. 125–126°. Calc. for $C_{19}H_{16}N_2$: C, 83.8; H, 5.9; N, 10.3%. Found : C, 83.7; H, 6.0; N, 10.5%

Reaction of titanium reagent (A) with benzaldehyde. The reagent (A; 0.04 mole) was reacted with benzaldehyde (1 ml; 0.01 mole) in E_2O for 0.5 hr at room temperature. After hydrolysis with dil HCl, the reaction mixture was extracted with Et_2O to give benzyl alcohol (23%), 1,2-diphenylethane-1,2-ethane-1,2-diol (60%) and benzaldehyde (16%).

Reaction of titanium reagent (A) with decene-1 epoxide. The reagent (A; 0.04 mole) was reacted with decene-1 epoxide (1.5 g; 0.01 mole) in Et_2O (25 ml) for 0.5 hr at room temperature. After hydrolysis and extraction with Et_2O, the product was examined by gc/ms and nmr which showed it to be a mixture of 1-chloro-2-decanol (70%) and 2-chloro-1-decanol (30%).

Preparation of Na/K alloy. The usual preparataion of Na/K alloys[19] is not made easy by the ease with which the surfaces of Na and K become readily coated with oxide/carbonate films which prevent the Na and K fusing readily. Frequently, the alloy forms as small spheres which will not coalesce. The preparation of Na/K alloys is made simple by addition of a crown ether. Thus, pieces of Na and K in a 1 : 3 molar ratio were melted in dry xylene under N_2 at 80° together with a few crystals of 18-crown-6. The Na/K alloy formed rapidly into one large shining metal ball which was liquid at room temperature and could be pipetted out for weighing.

Preparation of titanium reagent (D) with Na/K alloy. $TiCl_4$ (4.6 ml; 0.042 mole) in THF (100 ml) was reacted with Na/K alloy (Na : K, 1 : 3;3.05 g; 0.092 mole) at 40° for 3 h to give a black solution.

Preparation of titanium reagent (E) with Na/K alloy. The preparation was carried out as for reagent (D) but using only half the $TiCl_4$; a black solution was obtained.

Reduction of N-nitrosodiphenylamine with reagent (D) or (E). The reagent (D or E; from 0.042 mole $TiCl_4$) was reacted with N-nitrosodiphenylamine (1.98 g 0.01 mole) in THF at 25° for 15 min. After acid hydrolysis, the reaction mixture was made alkaline and extracted with Et_2O to give mainly (tlc, NMR) diphenylamine and a little N,N-diphenylhydrazine.

Reduction of N-nitrosodiphenylamine with titanium reagent [C; Ti(II) or Ti(O)]. prepared from $TiCl_4$ and $LiAlH_4$. $TiCl_4$ (0.3 ml; 0.003 mole) in THF (25 ml) was reacted with $LiAlH_4$ (0.035 g; 0.0015 mole) in THF under argon for 10 min with stirring. To this mixture was added N-nitrosodiphenylamine (0.198 g; 0.001 mole) in THF. After 15 min, the reaction mixture was hydrolysed with water and extracted with Et_2O to give diphenylamine together with a trace of starting material. Similarly, a Ti(O) reagent was prepared from $TiCl_4$(2.3 ml; 0.02 mole) and $LiAlH_4$ (0.8 g; 0.021 mole) and reacted with N-nitrosodiphenylamine (1.98g; 0.01 mole). On workup in the usual way, diphenylamine was the major product together with 15% of N,N-diphenylhydrazine, isolated as its benzylidene derivative.

Determination of nitrogen. After exposing the low-valent titanium reagents to nitrogen, the solutions were hydrolysed with dilute HCl(water : conc. HCl = 4 : 1 v/v) for 20 min and the organic layer separated. The aqueous layer was made alkaline and steam-distilled into an aqueous solution of boric acid; the distillate was titrated with 0.5 M HCl to determine NH_3. The accuracy of the method was checked against the standard, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\,H_2O$.

Preparation and reduction of ^{15}N-nitroso-N-methylaniline. N-Methylaniline (0.78 ml) was reacted with conc. HCl (1.02 ml) and to this acid solution was added dropwise a solution of $Na^{15}NO_2$ (0.5 g) in water (5 ml) with cooling in ice. After stirring the mixture for 1 hr, it was extracted with benzene to give N-^{15}N-nitroso-N-methylaniline (0.89 g; 92% yield); molecular ion, *m/z* 137 (isotopic purity > 98%). This nitroso compound (0.445 g; 0.0032 mole) in THF (5 ml) was added to the reducing reagent (A; 0.013 mole) and stirred for 20 min. The reaction mixture was hydrolysed with dil. HCl for 20 min at room temperature and then made alkaline. Extraction with diethyl ether gave crude N-methyl-N-phenylhydrazine which was converted to its benzylidene derivative m.107–108° (from EtOH). Calc. for $C_{14}H_{14}N_2$: C, 80.0; H, 6.7; N, 13.3%. Found : C, 79.8; H, 6.5; N, 13.5%. Molecular ion, *m/z* 211 (isotopic purity > 99%).

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