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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1992), 69(5-6): 489-494
Issue Date	1992-02-15
URL	http://hdl.handle.net/2433/77426
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

The Assistance of Electron-Withdrawing Group in the Reduction of C=N and C=O of Several Alkyl (Diphenylmethylene)-carbamates and Aromatic Ketones Using a Combination of Diphenylsilane and Aluminum Chloride

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Received September 19, 1991

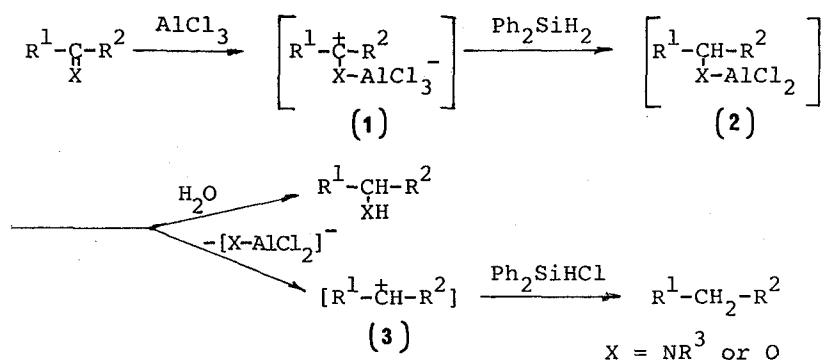
Several alkyl (diphenylmethylene)carbamates and *N*-(diphenylmethylene)-*p*-toluenesulfonamide were reduced to the corresponding alkyl (diphenylmethyl)carbamates or, in a few cases including the sulfonamide lastly described, hydrocarbon product, diphenylmethane in moderate yields by a combination of diphenylsilane and aluminum chloride in dichloromethane at room temperature. When aromatic ketones were submitted to this silicon hydride reduction, only several ketones bearing an electron-withdrawing group have been reduced to the corresponding alcohols and/or hydrocarbon products.

KEY WORDS: Diphenylsilane/ Aluminum chloride/ Reduction/ Alkyl (diphenylmethylene)carbamates/ Alkyl (diphenylmethyl)carbamates/ Diphenylmethane/ Aromatic ketones/

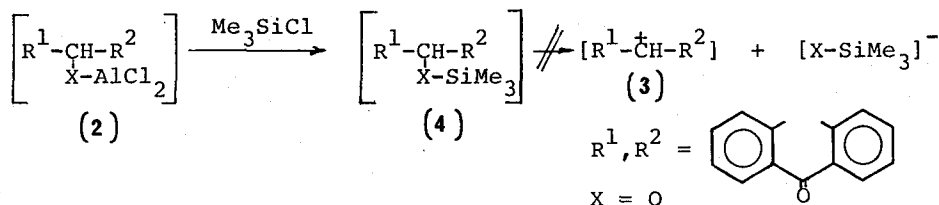
The silicon hydride reduction of the C=O group of aldehydes and ketones providing the corresponding alcohols or hydrocarbon products or, in less cases, alkyl silyl ethers has been found and reported in the literature. In these cases silicon hydrides such as triethylsilane or diphenylsilane have been employed together with one of KF (or CsF),¹⁾ trifluoroacetic acid,²⁾ concentrated hydrochloric acid (or aqueous sulfuric acid),³⁾ nickel (II) chloride [or ruthenium (II) chloride]⁴⁾ and gaseous boron trifluoride.⁵⁾ In the previous paper,⁶⁾ we have reported that α -keto esters and methyl *N-p*-tolylsulfonyl-2-aryl-2-iminoacetates are reduced to the corresponding α -hydroxy esters and methyl *N-p*-tolylsulfonyl-2-arylglycinates, respectively, in moderate to high yields by a combination of aluminum chloride and diphenylsilane. This suggests that the combination is fitted to the reduction of C=O group bearing an electron-withdrawing group. Also, the combination is able to reduce the C=N group bearing an electron-withdrawing group. In order to justify the suggestion, we have investigated the silicon hydride reduction of C=N and C=O of several alkyl (diphenylmethylene)carbamates and aromatic ketones bearing an electron-withdrawing group using the combination of diphenylsilane and aluminum chloride. In the previous paper,⁶⁾ we have employed 1.0 equivalent of aluminum chloride (based on the substrate) which was purchased and purified by sublimation. In the present work, however, 1.2 equivalents of aluminum chloride, which was purchased and not purified by sublimation, is used (see experimental section). The obtained results are summarized in Table I. As can be seen

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from Table I, the most remarkable feature of the present reaction is that the obtained products are only those derived by the hydrogenation with diphenylsilane. Except for butyl (diphenylmethylene)carbamate, alkyl (diphenylmethylene)carbamates have been reduced to the corresponding alkyl (diphenylmethyl)carbamates in moderate to high yields. Only butyl (diphenylmethylene)carbamate and *N*-(diphenylmethylene)-*p*-toluenesulfonamide have been reduced to the hydrocarbon product, namely diphenylmethane. It is not understandable why, only in these two cases, the formation of diphenylmethyl cation, which is generally formulated as $R^1-\overset{\oplus}{C}H-R^2$ (3) in Scheme 1, has been accelerated in the reaction system. When diphenylmethanimine was submitted to the silicon hydride reduction using the com-



Scheme 1



Scheme 2

ination of diphenylsilane and aluminum chloride, the formation of benzophenone in an almost quantitative yield has been recognized. Probably, initially formed diphenylmethanimine-aluminum chloride complex is hydrolyzed during the course of work-up procedure without undergoing hydride ion-transfer from diphenylsilane. This means that, in the silicon hydride reduction above-mentioned, the electron-withdrawing group such as alkoxy-carbonyl or *p*-tolylsulfonyl at the nitrogen of C=N assists the occurrence of reduction.

The same tendency also has been observed when the C=O group of acetophenone and its ring-substituted derivatives was reduced by the combination of diphenylsilane and aluminum chloride under the same reaction conditions. Although acetophenone failed to undergo such the silicon hydride reduction, 4'-nitroacetophenone and 1,4-diacetylbenzene underwent the same silicon hydride reduction. Thus, the former has been converted to a mixture of the corresponding hydrocarbon product, alcohol and alkyl silyl ether, and the latter

to the corresponding alcohol in a moderate yield (60%) together with a relatively small amount of the hydrocarbon product (4'-ethylacetophenone). In the case where 1,3-diacetylbenzene was used, a mixture of the corresponding alcohol and alkyl silyl ether was obtained. However, almost half amounts of starting 1,3-diacetylbenzene (48%) is recovered unaltered, suggesting that the electron-withdrawing effect of its *m*-CH₃CO group is less than that of the *p*-CH₃CO group of 1,4-diacetylbenzene.

In the previous paper,⁶⁾ we described that benzophenone fails to undergo the silicon hydride reduction using the combination of diphenylsilane and aluminum chloride. However, when we reexamined the reduction under the present reaction conditions, the formation of diphenylmethane in a low yield has been recognized (see Table I). 4-Nitrobenzophenone has been converted to 4-nitrodiphenylmethane in moderate yield by the reduction, suggesting that the *p*-NO₂ group effectively assists the hydride ion-transfer from diphenylsilane to the intermediate 1. When anthraquinone was submitted to the reduction, a mixture of anthrone (27%) and 10-hydroxy-9(10*H*)-anthracenone (38%) has been obtained. If 2.5 equivalents of chlorotrimethylsilane (based on anthraquinone) was added to the above reaction mixture in the beginning, the obtained product was only 10-hydroxy-9(10*H*)-anthracenone (50%). As is indicated in Scheme 2, the intermediate 2 would be converted to 4 by chlorotrimethylsilane, which would be difficult to decompose to R¹-CH-R² (3). If this procedure possesses the general applicability, it would become possible to reduce the aromatic ketones to the corresponding alcohols without any contamination with hydrocarbon products by the modified silicon hydride reduction. Acenaphthenequinone has been converted to a mixture of 1-acenaphthenone and 2-hydroxy-1-acenaphthenone. When these results are compared with that of benzophenone, accelerating effect by the neighboring electron-withdrawing group, which is included in the substrates, in the silicon hydride reduction is obvious.

By this silicon hydride reduction, furil has been converted to furoin in moderate yield (62%). 4,4'-Dimethyl- and 4,4'-dimethoxybenzil have been converted to 4,4'-dimethyl- and 4,4'-dimethoxybenzoin, respectively. But, both the yields were low. Probably, in these two cases, the silicon hydride reduction was retarded by the presence of the *p*-CH₃ or *p*-CH₃O group.

EXPERIMENTAL

General. The ¹H-NMR spectra were obtained on a Varian VXR-200 spectrometer in CDCl₃ with SiMe₄ as an internal standard. Alkyl (diphenylmethylene)carbamates were prepared according to the literature method.⁷⁾ *N*-(Diphenylmethylene)-*p*-toluenesulfonamide was prepared by the reaction of *N*-(trimethylsilyl)diphenylmethanimine with *p*-toluenesulfonyl chloride in anhydrous chloroform under a slight modification of the same literature method.⁷⁾ The starting substrates above-mentioned have been identified by their spectral and analytical data. Other starting substrates were purchased and used without further purification.

Reduction of Several Alkyl (Diphenylmethylene)carbamates and Aromatic Ketones Using a Combination of Diphenylsilane and Aluminum Chloride (General Procedure). To a solution of one of substrates (1.0 mmol) in dichloromethane (10 ml) was added under nitrogen

aluminum chloride (0.16 g, 1.2 mmol) at room temperature. The mixture was stirred at the same temperature for 2 h or more to make it homogeneous. Then, diphenylsilane (0.223 ml, 1.2 mmol) was added to the mixture. This was followed by stirring at room temperature for 24 h. The mixture was poured into water (10 ml) and extracted with dichloromethane (3×10 ml). The combined extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo* to give a residue, which was subjected to column chromatography on silica gel using 20% ethyl acetate-80% hexane as eluent.


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Table I. Reduction of Alkyl (Diphenylmethylene)carbamates and Aromatic Ketones Using a Combination of Diphenylsilane and Aluminum Chloride

Run	Starting substrate	Product ^{a)} (Yield/%)	Mp (°C) or Bp (°C/mmHg)	¹ H-NMR (δ in CDCl ₃)	Recovered substrate/%
1	Ph ₂ C=NCO ₂ Me	{ Ph ₂ CHNHCO ₂ Me (96) Ph ₂ CH ₂ (4)	144–145 (lit. ⁸⁾ 141–143)	3.68(s, 3H), 5.2–5.5(m, 1H), 5.8–6.1(m, 1H), 7.1–7.5(m, 10H)	0
2	Ph ₂ C=NCO ₂ Et	{ Ph ₂ CHNHCO ₂ Et(66) Ph ₂ CO ^{b)} (32)	126–127 (lit. ⁹⁾ 128–129)	1.23(t, 3H, <i>J</i> =2.1Hz), 4.13(q, 2H, <i>J</i> =2.1Hz), 5.2–5.5(m, 1H), 5.8–6.1(m, 1H), 7.1–7.5(m, 10H)	0
3	Ph ₂ C=NCO ₂ Bu ⁱ	Ph ₂ CHNHCO ₂ Bu ⁱ (54)	84–86 (lit. ¹⁰⁾ 89–90)	0.6–1.1(m, 6H), 1.7–2.1(m, 1H), 3.86(d, 2H, <i>J</i> =2.0Hz), 5.1–5.5(m, 1H), 5.8–6.1(m, 1H), 7.1–7.6(m, 10H)	11
4	Ph ₂ C=NCO ₂ (CH ₂) ₄ Me	{ Ph ₂ CHNHCO ₂ (CH ₂) ₄ Me(67) Ph ₂ CO ^{b)} (12)	58–58.5	0.8–1.0(m, 3H), 1.1–1.5(m, 4H), 1.5–1.8(m, 2H), 4.07(t, 2H, <i>J</i> =2.0Hz), 5.2–5.5(m, 1H), 5.8–6.1(m, 1H), 7.1–7.5(m, 10H)	13
5	Ph ₂ C=NCO ₂ Bu ⁿ	Ph ₂ CH ₂ (51)			37
6	Ph ₂ C=NSO ₂ C ₆ H ₄ Me(<i>p</i> -)	Ph ₂ CH ₂ (83)			17
7	<i>p</i> -NO ₂ C ₆ H ₄ COMe	{ <i>p</i> -NO ₂ C ₆ H ₄ Et(18) <i>p</i> -NO ₂ C ₆ H ₄ CH(Me)OH(18) <i>p</i> -NO ₂ C ₆ H ₄ CH(Me)OSiHPh ₂ ^{c)} (34)	118/2–3 (lit. ¹¹⁾ 158/16) Bp was not measured.	1.65(d, 3H, <i>J</i> =2.2Hz), 4.22 (1, 1H, <i>J</i> =2.2Hz), 6.9–8.3(m, 4H) 1.68(d, 3H, <i>J</i> =2.2Hz), 4.26 (1, 1H, <i>J</i> =2.2Hz), 7.1–8.3(m, 14H,)	0
8	<i>p</i> -MeCOC ₆ H ₄ COMe	{ <i>p</i> -MeCOC ₆ H ₄ Et(11) <i>p</i> -MeCOC ₆ H ₄ CH(Me)OH(60)	150/2–3 (lit. ¹²⁾ 118–120/0.4)	1.83(d, 3H, <i>J</i> =2.0Hz), 2.58 (s, 3H, 5.09(q, 1H, <i>J</i> =2.0Hz), 7.3–8.1(m, 4H)	24

Table I. continued.

Run	Starting substrate	Product ^{a)} (Yield/%)	Mp (°C) or Bp (°C/mmHg)	¹ H-NMR (δ in CDCl ₃)	Recovered substrate/%
9	<i>m</i> -MeCOC ₆ H ₄ COMe	$\left\{ \begin{array}{l} m\text{-MeCOC}_6\text{H}_4\text{CH}(\text{Me})\text{OH}^{\text{d)}} (29) \\ [\text{Ph}_2\text{HSiOCH}(\text{Me})]_2 \text{C}_6\text{H}_4^{\text{e)}} (17) \end{array} \right.$ 	Bq was not measured. Mp was not measured.	1.44(d, 3H, <i>J</i> =1.9Hz), 2.60(s, 3H), 4.35(q, 1H, <i>J</i> =1.9Hz), 7.0–8.1(m, 4H) 1.44(d, 3H, <i>J</i> =2.0Hz), 1.86(d, 3H, <i>J</i> =2.0Hz), 4.31(q, 1H, <i>J</i> =2.0Hz), 5.10(q, 1H, <i>J</i> =2.0Hz), 6.9–7.8(m, 24H)	48
10	Ph ₂ CO	Ph ₂ CH ₂ (12)			80
11	<i>p</i> -NO ₂ C ₆ H ₄ COPh	<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Ph(65)	25–28 (lit. ¹³⁾ 31)	4.09(s, 2H), 7.2–8.2(m, 9H)	34
12 ^{e)}	Anthraquinone	$\left\{ \begin{array}{l} \text{Anthrone}(27) \\ 10\text{-Hydroxy-}9(10H)\text{-} \\ \text{anthracenone}(38) \end{array} \right.$	155–158 (lit. ¹⁴⁾ 156–157)	4.77(s, 1H), 6.8–8.0(m, 8H)	34
13	Acenaphthenequinone	$\left\{ \begin{array}{l} 1\text{-Acenaphthenone}(6) \\ 2\text{-Hydroxy-}1\text{-} \\ \text{acenaphthenone}(21) \end{array} \right.$	117–120 (lit. ¹⁵⁾ 121–123) 150–153 (lit. ¹⁶⁾ 156–157)	3.83(s, 2H), 7.1–8.3(m, 6H) 5.38(s, 1H), 6.9–8.7(m, 6H)	45
14	Furil	Furoin(62)			12
15	4,4'-Dimethylbenzil	4,4'-Dimethylbenzoin(16)			73
16	4,4'-Dimethoxybenzil	4,4'-Dimethoxybenzoin(17)			57

- a) The products of which the description concerning physical properties is omitted are commercially available.
- b) Initially formed substrate-aluminum chloride complex is hydrolyzed during the course of work-up procedure.
- c) In the ¹H-NMR spectrum of this compound, the signal which is attributed to the proton of Si-H could not be found. Then, the compound has been identified further with the help of mass spectrum.
- d) Known compound. But, the description concerning its physical property could not be found.
- e) When the amount of diphenylsilane was changed to 2.2 equivalents from 1.2 equivalents per substrate without being changed the amount of aluminum chloride and the reaction conditions, the yield of anthron was 30% and that of 10-hydroxy-9(10*H*)-anthracenone was 19%. When, in Run 12, 2.5 equivalents of chlorotrimethylsilane (based on the substrate) was added initially to the reaction mixture, the obtained product was only 10-hydroxy-9(10*H*)-anthracenone(50%).