

2,3,4,5-Tetrahydro-2,4-diimino-1,3,5-triazin-1-ium salts in the reaction of carbodiimides with *N*-alkylnitrilium salts

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Abstract

2,3,4,5-Tetrahydro-2,4-diimino-1,3,5-triazin-1-ium hexachloroantimonate salts were formed by the addition of carbodiimides to *N*-alkylnitrilium salts. The compounds were characterized using microanalytical and spectroscopic (IR, MS, and NMR) data.

Keywords: Carbodiimides, nitrilium salts, 1,3,5-triazinium salt, cycloaddition

Introduction

The existence of nitrilium salts **1** (Figure 1) was predicted and nitrilium salts were proposed as intermediates in organic synthesis and reaction mechanisms by Hantzsch¹ in 1931. Stable nitrilium salts, **1**, were first prepared by Klages² and Meerwein.³⁻⁵

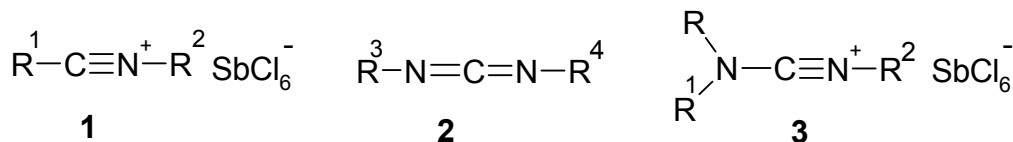
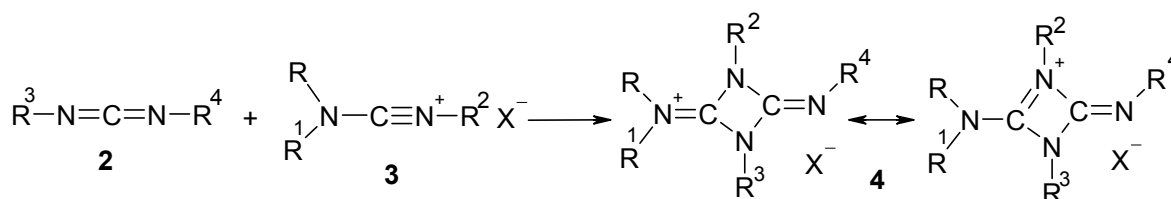


Figure 1

The dipolarophilicity of the nitrile moiety is only moderate.⁶ However, electron-withdrawing substituents or Lewis acid catalysis enhance the reactivity of nitriles towards nucleophiles and 1,3-dipolar species.^{6,7} Thus, nitrilium salts react smoothly with a variety of nucleophiles and 1,3-dipoles. Cycloadditions of organic azides to nitrilium salts **1** lead to trisubstituted tetrazolium salts.⁸⁻¹¹ These reactions are dominated by a concerted mechanism.⁹ However, the cycloaddition of the azide ion N_3^- to nitrilium ions is assumed to proceed *via* a two-step mechanism.⁹⁻¹³ Previously, we reported the synthesis of 1,2,4-oxadiazonium salts by the cycloaddition of nitrile oxides to nitrilium and cyanamidium salts.¹⁴ Also, the addition of nitrilium salts to α,β -unsaturated carbonyl compounds led to the formation of 4*H*-1,3- and 6*H*-1,3-oxazinium salts

through a multistep reaction sequence starting with a [2+2] cycloaddition involving the carbonyl π -bond and the nitrilium functionality.¹⁵ Tetrahydrotriazinium and 2-azonia-allene salts were formed as a result of [2+2+2] cycloaddition of *N*-alkylimines to nitrilium- and cyanamidium salts,¹⁶ while the azonia-allene salts were formed by 1-5 hydrogen shift. Abramovitch *et al.*,¹⁷⁻²⁰ and Jochims *et al.*²¹ reported the cycloaddition of heterocyclic nitrones to nitrilium salts, which was reviewed recently.²² 3,4-Bis-(methylthio)-2*H*-pyrrolium salts and 2-azonia-allenes were formed by the addition of nitrilium salts to bis-(methylthio)acetylene²³ through the formation of 2-azonia-allene salts by a 1-5 hydrogen shift followed by cyclization. Moreover, 2,3,4,5-tetrahydro-1,3,5-triazinium salts were obtained by the addition of *N*-substituted imines to nitrilium salts **1**.²⁴ The formation of symmetrical and asymmetrical *N*-[4-imino-1,3-diazetidino-2-ylidene]aminium hexachloroantimonate salts **4**, as geometrical isomerization products upon the addition of carbodiimides **2** to cyanamidium salts **3** (shown in Scheme 1), have been reported quite recently.²⁵



Scheme 1. Reaction of cyanamidium salts **3** and carbodiimides **2**.

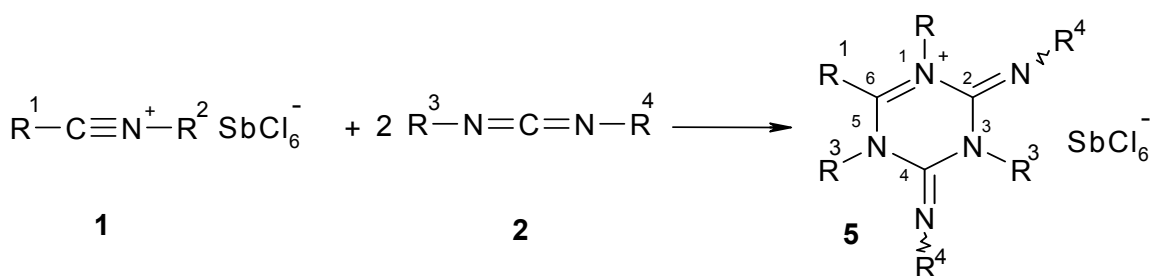
As part of ongoing studies related to of the synthesis and reactions of nitrilium-, **1**, and cyanamidium, **2**, salts,^{14-16, 23-28} the reaction of carbodiimides **2** with *N*-alkylnitrilium salts **1** is reported herein, along with the resulting derivatives (Scheme 2), and their characterization.

Results and Discussion

The addition of the carbodiimides **2a–d** to a solution of *N*-alkylnitrilium salts **1a–f** in dichloromethane at low temperature afforded the triazinium salts **5a–i** in 45–91% yield. It is suggested that the compounds **5a–i** are formed through a [2+2+2]- cycloaddition, in analogy to the formation of cycloadducts by the reaction of nitrilium salts with *N*-substituted imines.²⁵ The reaction involves the formation of intermediate **6** (1:1 adduct) which reacts further with another mole of the carbodiimide **2** (Scheme 3).

The structures of the newly prepared triazinium salts **5a–i** are derived from elemental analyses, and IR- and NMR- spectral data that are given in the Experimental Part. It is worth noting that the ¹H- NMR spectrum of **5e** in CD₃CN shows four signals for different isopropyl groups, and only one *N*-methyl group at $\delta = 3.01$. Considerable line broadening of the ¹³C-signal of the *N*-methyl resonance indicates slow geometrical isomerization of the exocyclic C²=N and

C⁴=N double bonds. Also, the ¹³C-NMR spectrum shows signals at $\delta = 137.4$, 140.7 and 165.5 ppm which are attributed to C²=N, C⁴=N and C⁶=N⁺, respectively. The IR spectrum of **5e** in CH₂Cl₂ shows stretching absorption peaks at 1690, 1650, 1540 and 1500 cm⁻¹ corresponding to different types of imines and iminium cation. The formation of only one isomer for **5i** can be explained by the preferred nucleophilicity of *N*-methyl- over the *N*-*tert*-butyl group as a result of the steric effect of the latter group. A similar assumption was reported for the addition of carbodiimides to cyanamidium salts,²⁵ and in the dimerization of carbodiimides in the presence of alkylating reagents.²⁹⁻³³ Geometrical isomerization was also observed in the ¹³C-NMR of some compounds such as **5i** and **5j**.

Compounds **1a-h**

Entry	a	b	c	d	e	f
R ¹	Me	Et	<i>i</i> -Pr	Bz	Ph	Ph
R ²	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	Me

Compounds **2a-d**

Entry	a	b	c
R ³	<i>i</i> -Pr		Me
R ⁴	<i>i</i> -Pr		<i>t</i> -Bu

Compounds **5a-i**

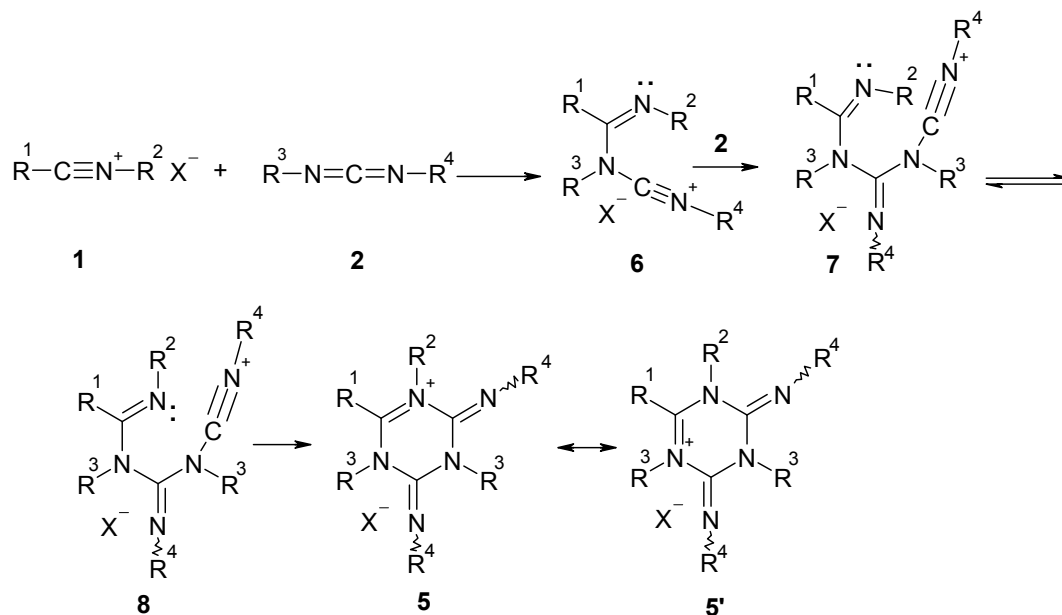
Entry	a	b	c	d	e	f	g	h	i
R ¹	Me	Et	<i>i</i> -Pr	<i>i</i> -Pr	Ph	Bz	Ph	Ph	Ph
R ²	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	Me	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr
R ³	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr		<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr		Me
R ⁴	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr		<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr		<i>t</i> -Bu

Scheme 2. Synthesis of 1,3,5-triazinium salts, **5**.**Mechanism**

The nucleophilic addition to nitrilium ions has been reported by Hegarty and his co-workers.²⁹ to be stereo-electronically controlled. The nitrogen lone-pair always develops *anti*- to the intruding nucleophile (*Z*-isomer). In the resulting imines, the nucleophile and the *N*-substituent are *syn*-oriented with respect to each other. It is likely, therefore, that the addition of the carbodiimide **2**

to a nitrilium ion **1** gives the (*Z*) adduct as the primary product. Thermal isomerization around the R-C=N-R bond furnishes the (*E*) form, which may readily undergo ring closure.

The formation of **5** by the addition of the carbodiimide **2** to the nitrilium salt **1** is believed to be due to stepwise polar cycloadditions.^{29,30} This involves the addition of two moles of carbodiimides **2** (added in two successive additions) *via* the formation of new cyanimidium salts **6** and **7** (Scheme 3). The latter intermediate, **7**, isomerizes to the (*E*)- geometrical isomer **8**, followed by ring closure to form the [2+2+2] cycloadduct, salt **5**. This pathway is in contrast to the formation of a [2+2] cycloadduct, as in the case of dimerization of carbodiimides,²⁹⁻³¹ and the case of the addition of carbodiimides to cyanamidium salts.²⁵ The driving force for the second addition of another molecule of carbodiimide **2** to form **5** (instead of ring closure to diazetidinium salts) is presumably due to the formation of a resonance stabilized [2+2+2] adduct (**5**↔**5'**).



Scheme 3. Proposed mechanism for the formation of compounds **5**.

Experimental Section

General Procedures. All experiments were carried out with the exclusion of moisture, in solvents dried by standard methods. Melting points were determined with Electrothermal 9100 apparatus and have not been corrected. The ¹H- and ¹³C-NMR spectra were recorded on Bruker AC-250 and Bruker DPX-300 instruments, using TMS as internal standard, and with deuterated chloroform, dichloromethane or acetonitrile as the solvent; chemical shifts (δ) are in ppm and coupling constants (*J*) in Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR in CH₂Cl₂ solution; the frequencies are expressed in cm⁻¹. Elemental microanalyses were obtained on an

Elemental Analyzer (Carlo Erba 1106) from vacuum-dried samples. The nitrilium salts **1a**,²⁸ **1b**,²³ **1c**,²⁸ **1d**,³⁴ **1e**,⁴ and **1f**,² were prepared according to literature procedures.

General procedure for preparation of substituted 2,3,4,5-tetrahydro-2,4-diimino-1,3,5-triazin-1-ium hexachloroantimonate, 5a-i

A solution of 10 mmol of the carbodiimide **1a-c** dissolved in 20 mL of dichloromethane was added dropwise to a cooled (-20 °C), stirred solution of 5 mmol of the appropriate nitrilium hexachloroantimonate **2a-f**. The solution was stirred at this temperature for 1 h, then allowed to rise to 10 °C and stirred for an additional 1 h, after which time the IR of the solution showed the disappearance of the absorption of the nitrilium peak of the nitrilium salts (2230 cm⁻¹). The reaction solution was reduced to half volume *in vacuo*, then cooled to -20 °C, then 100 mL of absolute diethyl ether was added dropwise to give a powder precipitate, which was collected under vacuum and dried. The precipitate was purified by recrystallization from 10 mL/100 mL diethyl ether.

1,3,5-Tri-isopropyl-2,4-di-isopropylimino-6-methyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5a). White solid (70 %); mp 108-110 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 3051, 2968, 1774, 1716; ¹H NMR (300 MHz, CD₃CN): δ 1.19 (d, *J* = 6.9 Hz, 12H, 2x(CH₃)₂CH), 1.25 (d, *J*=6.9 Hz, 6H, (CH₃)₂CH), 1.57 (d, *J* 6.9 Hz, 12H, 2x(CH₃)₂CH), 2.69 (s, 3H, CH₃), 3.25 (sept., *J* 6.9 Hz, 2H, (CH₃)₂CH), 4.28 (sept., *J* 6.9 Hz, 1H, (CH₃)₂CH), 4.568 (sept., *J* 6.9 Hz, 2H, 2(CH₃)₂CH); ¹³C NMR (75 MHz, CD₃CN): δ (ppm) 20.8, 21.4, 22.7, 24.9, 50.6, 55.5, 56.6, 136.2, 136.3, 167.6. Anal. Calcd. for C₁₉H₃₈N₅SbCl₆ (671.0): C, 34.01; H, 5.71; N, 10.44. Found: C, 34.19; H, 5.68; N, 10.23%.

6-Ethyl-1,3,5-tri-isopropyl-2,4-di-isopropylimino-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5b). White solid (66%); mp 125-128°C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690 (w), 1655 (m), 1520 (s). ¹H NMR (300 MHz, CD₃CN): δ (ppm) 1.13 (d, *J* 6.9 Hz, 12H, 2(CH₃)₂CH), 1.22 (d, *J* 6.9 Hz, 6H, (CH₃)₂CH), 1.35 (d, *J* 7.3 Hz, 3H, CH₃CH₂), 1.56 (d, *J* 6.9 Hz, 12H, 2(CH₃)₂CH), 2.94 (q, *J* 7.3 Hz, 2H, CH₃CH₂), 3.15 (sept., *J* 6.9 Hz, 2H, 2(CH₃)₂CH), 4.36 (sept., *J* 6.9 Hz, 1H, (CH₃)₂CH), 4.58 (sept., *J* 6.9 Hz, 2H, 2(CH₃)₂CH). ¹³C NMR (75 MHz, CD₃CN): δ (ppm) 11.8, 20.3 (br), 21.2, 23.5, 24.7, 50.6, 55.6, 56.7, 136.3, 136.4, 167.5. Anal. Calcd. for C₂₀H₄₀N₅SbCl₆ (685.1): C, 35.07; H, 5.89; N, 10.22. Found: C, 35.22; H, 5.67; N, 10.38%.

1,3,5,6-Tetra-isopropyl-2,4-di-isopropylimino-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5c). White solid (53%); mp 137-139°C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1700, 1650, 1600 (w), 1525 (s), 1400 (br), 1370, 1200, 1100. ¹H NMR (CDCl₃): δ 1.21 (d, 12H, *J* 7.0 Hz, 2(CH₃)₂CH), 1.65 (3d, 18H, *J* 7.0 Hz, 3(CH₃)₂CH), 1.8 (d, 6H, *J* 7.0 Hz, (CH₃)₂CH), 3.18 (sept., 2H, *J* 7.0 Hz, 2(CH₃)₂CH), 3.87 (sept., 1H, *J* 7.0 Hz, (CH₃)₂CH), 4.30 (sept., 2H, *J* 7.0 Hz, 2(CH₃)₂CH), 4.97 (sept., 1H, *J* 7.0 Hz, (CH₃)₂CH). ¹³C NMR (CDCl₃): δ 19.5, 20.9, 21.9, 23.3, 30.7, 50.6, 55.23, 56.3, 137.5, 137.6, 172.5. Anal. Calcd. for C₂₁H₄₂N₅SbCl₆ (699.1): C, 36.05; H, 6.06; N, 10.02. Found: C, 35.99; H, 5.92; N, 9.91%.

3,5-Dicyclohexyl-2,4-dicyclohexylimino-1,6-di-isopropyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5d). White solid (45 %); mp 139-141 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690, 1660, 1600 (w), 1520 (s), 1400 (br), 1200. ¹H NMR (CDCl₃): δ 1.21-1.82 (m, 20H), 1.67 (d, 6H, *J* 6.9 Hz, (CH₃)₂CH), 1.75 (d, 6H, *J* 6.9 Hz, (CH₃)₂CH), 2.42 (m, 2H), 2.66 (m, 1H), 3.93 (m, 2H), 4.40 (m, 1H). ¹³C NMR (CDCl₃): δ 128.6, 137.2, 157.1, and others; the spectrum changed during measurements. Anal. Calcd. for C₃₃H₅₈N₅SbCl₆ (859.3): C, 46.12; H, 6.80; N, 8.15. Found: C, 46.22; H, 7.05; N, 7.92%.

3,5-Di-isopropyl-2,4-di-isopropylimino-1-methyl-6-phenyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5e). White solid (63 %); mp 158-161 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690 (m), 1650 (s), 1540 (s), 1500 (w), 1400 (br). ¹H NMR (CD₃CN): δ 1.14 (d, 6H, *J* 7.0 Hz, (CH₃)₂CH), 1.24 (d, 6H, *J* 7.0 Hz, (CH₃)₂CH), 1.48 (d, 6H, *J* 7.0 Hz, (CH₃)₂CH), 1.97 (d, 6H, *J* 7.0 Hz, (CH₃)₂CH), 3.01 (s, 3H, CH₃), 3.54 (sept., 1H, *J* 6.9 Hz, (CH₃)₂CH), 3.94 (sept., 1H *J* 6.9 Hz, (CH₃)₂CH), 4.30 (sept., 1H, *J* = 7.0 Hz, (CH₃)₂CH), 4.40 (sept., 1H, *J* = 6.9 Hz, (CH₃)₂CH), 7.54-7.78 (m, 5H). ¹³C NMR (CD₃CN): δ 19.4, 21.4, 22.6, 23.31, 23.6, 24.1, 38.8 (CH₃-N⁺), 50.4, 51.1, 57.7, 59.2, 118.4, 126.6, 126.7, 127.8, 131.1, 133.4, 137.4, 140.7, 165.5. Anal. Calcd. for C₂₂H₃₆N₅SbCl₆ (705.1): C, 37.48; H, 5.15; N, 9.93. Found: C, 37.59; H, 5.34; N, 9.75%.

6-Benzyl-1,3,5-tri-isopropyl-2,4-di-isopropylimino-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5f). Yellow solid (67 %); mp 115-120 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690 (w), 1650, 1590, 1520 (s). ¹H NMR (CD₃CN): δ 1.18 (d, 12H, *J* = 6.9 Hz, 2(CH₃)₂CH), 1.21 (d, 6H, *J* = 6.9 Hz, (CH₃)₂CH), 1.49 (d, 6H, *J* 6.9 Hz, 2(CH₃)₂CH), 3.31 (sept., 2H, *J* 6.9, 2(CH₃)₂CH), 4.36 (sept., 2H, *J* 6.9 Hz, 2(CH₃)₂CH), 4.42 (s, 2H, CH₂), 4.47 (m, 2H, 2(CH₃)₂CH), 7.26 (m, 2H), 7.50 (m, 3H); ¹³C NMR (CD₃CN): δ 21.1(br), 21.4, 23.5, 36.5, 50.7, 55.5, 57.7, 128.3, 129.2, 130.6, 131.9, 132.0, 138.0, 166.2. Anal. Calcd. for C₂₅H₄₂N₅SbCl₆ (747.12): C, 40.19; H, 5.67; N, 9.38. Found: C, 40.24; H, 5.44; N, 9.21%.

1,3,5-Tri-isopropyl-2,4-di-isopropylimino-6-phenyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5g). White solid (91 %); mp 166-168 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690 (w), 1660, 1510 (s), 1400. ¹H NMR (CD₃CN): δ 1.21(d, 12H, *J* 5.7 Hz, 2(CH₃)₂CH); 1.27 (d, 6H, *J* 6.4 Hz, (CH₃)₂CH); 1.41(d, 6H, *J* 6.0 Hz,); 3.47 (sept., 2H, *J* 6.4 Hz, 2(CH₃)₂CH); 3.86 (sept., 1H, *J* 6.7 Hz, (CH₃)₂CH); 4.40 (sept., 2H, *J* 6.2 Hz, 2(CH₃)₂CH); 7.71 (m, 3H); 7.74 (m, 2H); ¹³C NMR (CD₃CN): δ 21.4, 21.5, 23.5, 51.0, 56.9, 59.6, 126.4, 128.3, 131.5, 133.4, 133.5, 137.9, 165.8. Anal. Calcd. for C₂₄H₅₆N₅SbCl₆ (733.1): C, 39.32; H, 5.50; N, 9.55. Found: C, 39.42; H, 5.67; N, 9.56%.

3,5-Dicyclohexyl-2,4-dicyclohexylimino-1-isopropyl-6-phenyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5h). White solid (63 %); mp 159-161 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹): 1690 (w), 1650 (m), 1600 (w), 1400 (br); ¹³C NMR (CDCl₃): δ 23.8, 23.9, 24.7, 25.0, 25.1, 25.6, 26.1, 31.3, 33.2, 58.3, 58.4, 59.1, 63.4, 67.43, 125.3, 126.5, 131.1, 133.0, 136.0, 136.3, 165.0. Anal. Calcd. for C₃₆H₅₆N₅SbCl₆ (893.3): C, 48.40; H, 6.32; N, 7.70. Found: C, 48.19; H, 6.49; N, 7.70%.

2,3-Di-tert-butylimino-1-isopropyl-3,5-dimethyl-6-phenyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium hexachloroantimonate (5i). White solid (64 %); mp 137-139 °C; IR (CH₂Cl₂) ν_{\max} (cm⁻¹):

1700, 1670, 1600, 1550, 1400 (br). ¹H NMR (CD₂Cl₂): δ 1.44 (s, 9H, (CH₃)₃C), 1.47 (d, 6H, *J* = 6.8 Hz, (CH₃)₂CH), 1.49 (s, 9H, (CH₃)₃C), 3.08 (s, 3H, CH₃), 3.23 (s, 3H, CH₃), 3.97 (sept., 1H, *J* 6.8 Hz, (CH₃)₂CH), 7.49-7.78 (m, 5H). ¹³C NMR (CD₂Cl₂): δ 21.8, 29.2, 29.8, 30.6, 31.2, 39.4, 45.7, 56.0, 57.6, 58.9, 126.5, 127.4, 127.9, 129.2, 131.0, 133.1, 133.3, 133.4, 134.5, 165.4; Anal. Calcd. for C₂₁H₄₂N₅SbCl₆ (699.1): C, 36.08; H, 6.06; N, 10.02. Found: C, 35.99; H, 5.92; N, 9.91%.

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References

1. Hantzsch, A. *Ber.* **1931**, *64*, 667.
2. Klages, F.; Grill, W. *Liebigs Ann. Chem.* **1955**, *594*, 21.
3. Meerwein, H. *Angew. Chem.* **1955**, *67*, 374.
4. Meerwein, H.; Laasch, H.; Mersch, R.; Spille, J. *Chem. Ber.* **1956**, *89*, 209.
5. Meerwein, H.; Laasch, H.; Mersch, R.; Nentwig, J. *Chem. Ber.* **1956**, *89*, 224.
6. Bast, K.; Christl, M.; Huisgen, R.; Mack, M. *Chem. Ber.* **1972**, *105*, 2825.
7. Chang, M. S.; Lowe, J. U. *J. Org. Chem.* **1967**, *32*, 1577 (1967).
8. Morrocchi, S.; Ricca, A.; Velo, L. *Tetrahedron Lett.* **1967**, *8*, 331.
9. Quast, H.; Bieber, L. *Tetrahedron Lett.* **1976**, *17*, 1485.
10. Quast, H.; Bieber, L.; Meichsner, G. *Chem. Ber.* **1987**, *120*, 469.
11. Artamonova, T. V.; Zhivich, A. V.; Dubinskii, M. Yu.; Koldobskii, G. I. *Synthesis* **1996**, 1428.
12. Carboni, B.; Carrie, R. *Tetrahedron* **1984**, *40*, 4115.
13. Kevill, D. N.; Weitzel, F. L. *J. Org. Chem.* **1970**, *35*, 2526.
14. Abu-El-Halawa, R.; Shrestha-Ddwadi, P. B.; Jochims, J. C. *Chem. Ber.* **1993**, *126*, 107.
15. Abu-El-Halawa, R.; Glocker, M. O.; Zsolnai, L.; Huttner, G.; Jochims, J. C. *Synthesis* **1990**, 763.
16. Abu-El-Halawa, R. *Al-Manarah* **1999**, *4*, 189.
17. Abramovitch, R. A.; Singer, G. M. *J. Am. Chem. Soc.* **1969**, *91*, 5672.
18. Abramovitch, R. A.; Rogers, R. B. *Tetrahedron Lett.* **1971**, *12*, 1951.
19. Abramovitch, R. A.; Singer, G. M. *J. Org. Chem.* **1975**, *39*, 1795.

20. Abramovitch, A.; Shinkai, I. *Acc. Chem. Res.* **1976**, *9*, 192.
21. Hitzler, M. G.; Freyhardt C. C.; Jochims, J. C. *J. Prakt. Chem. Chemikar-Zeitung* **1996**, *338*, 243.
22. Youssif, S. *ARKIVOC* **2001**, (*i*), 242.
23. Abu-El-Halawa, R.; Jochims, J. C. *Synthesis* **1992**, 871.
24. Abu-El-Halawa, R. *Al-Manarah* **1998**, *3*, 53.
25. Abu-El-Halawa, R. *J. Saudi Chem. Soc.* **2008**, *12*, in press.
26. Abu-El-Halawa, R.; Wirschum, W.; Mustafa, H.; Jochims, J. C. *J. Prakt. Chem.* **1996**, *338*, 598.
27. Mustafa, A. H.; Abu-El-Halawa, R.; Wirschum, W. Jochims, J. C. *J. Prakt. Chem.* **1997**, *339*, 615.
28. Jochims, J. C.; Abu-El-Halawa R. *Chem. Ber.* 1984, *117*, 1900.
29. Hegarty, A. F. *Acc. Chem. Res.* **1980**, *13*, 448, and references cited therein.
30. Schmidt R. R. *Angew. Chem.* **1973**, *85*, 235, *Angew. Chem. Int. Ed.* **1973**, *12*, 212.
31. Hartke, K.; Rossbach, F.; Radau, M. *Liebigs Ann. Chem.* **1972**, *762*, 167.
32. Hartke, K.; Rossbach, F.; Radau, M. *Angew. Chem.* **1968**, *80*, 83; *Angew. Chem. Int. Ed.* **1968**, *7*, 72.
33. Scheffold, R.; Saladin, E. *Angew. Chem.* **1972**, *84*, 158; *Angew. Chem. Int. Ed.* **1972**, *11*, 229.
34. Jochims, J. C.; Abu-El-Halawa, R. *Synthesis* **1990**, 488.