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Synthesis of Formazan-3-yltriazolium Salts: A New Class of Formazan and Crown-formazan Derivatives of Expected Useful Applications.

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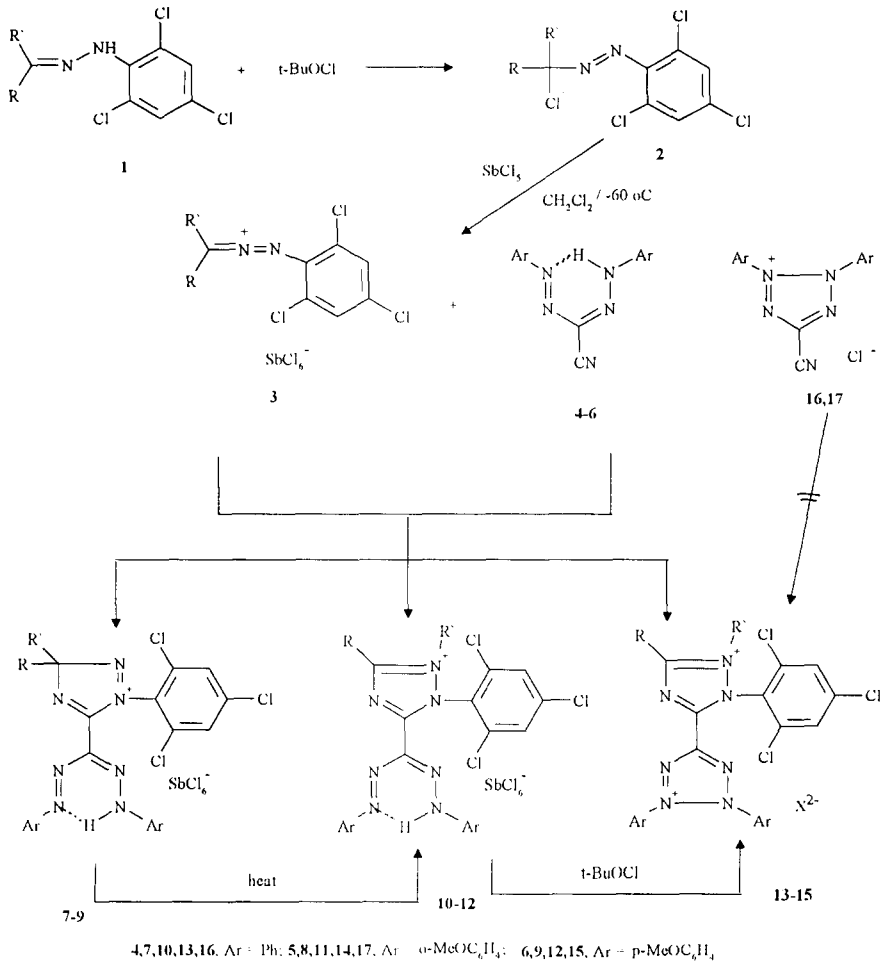
Abstract: The 1-aza-2-azoniaallene salts **3** react with 3-cyanoformazans **4-6** to give the corresponding 5-(1,5-diarylformazan-3-yl)triazolium salts **7-9** or the rearrangement derivatives **10-12** or the oxidation products **13-15**. Reaction of **3a,d** with the crown cyanoformazan **18** gave the corresponding crown-formazanyltriazolium salts **19a,d**. Oxidation of the formazans **4**, **10b** with t-BuOCl afforded the corresponding tetrazolium salts **16**, **13b**.

INTRODUCTION

The wide applications of formazans have been the subject of a large number of publications which were cited previously.[1] They have been used as potential chromogenic chelates for transition metals and post-transition metals. Also, crown-formazans have attracted special recent interest due to their applications in selective metal ion extraction and microdetermination.[1-3] There are limited ways of introducing functional groups which seems to confer special properties on this class of compounds at the 3-position in these formazans. The recently reported in situ preparation of 1-aza-2-azoniaallene salts (e.g. **3**) and their cycloaddition to multiple bonds of olefins,[4] acetylenes,[4,5] carbodiimides,[4,6] isocyanates[4,7] and nitriles[4,8] to give five membered heterocycles stimulated the present synthetic approach toward a new class of formazans substituted with triazolium cation at the 3-position with possible interesting applications.

RESULTS AND DISCUSSIONS

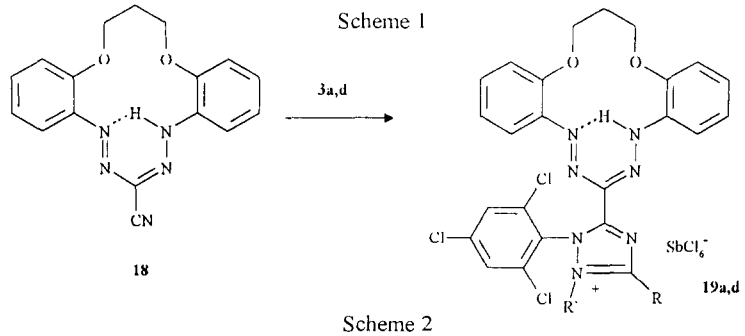
Recently, many ketone arylhydrazones **1** were oxidized to the corresponding α-chloroazo compounds **2** which upon treatment at low temperature with $SbCl_5$ gave the corresponding 1-aza-2-azoniaallene salts **3**.[4-8] In this paper the reaction of **3** with the 3-cyanoformazans **4-6** was investigated as a possible synthetic route toward the formazanyl-1,2,4-triazolium salts **7-9, 10-12** (Scheme 1). Thus, addition of $SbCl_5$ to an equimolecular solution of 1-[(1-chloro-1-methylethyl)azo]-2,4,6-trichlorobenzene **2a** and 3-cyano-1,5-diphenylformazan **4** in dichloromethane (as described for other nitriles)[8] produced low yield (ca. 20%) of the corresponding triazolium salt **10a**. However, compound **10a** was obtained in ca. 70% yield when compound **4** was added to the freshly prepared salt **3a** at -60°C. It was therefore apparent that this sequence of reaction overcame the destruction of the chloroazo compound through possible oxidation of the formazans into the corresponding tetrazolium salts and also the decomposition of the reagents **3** by the formazan acidic proton. This assumption is substantiated by the fact that when compound **5** was treated similarly, the corresponding triazolium derivative **11a** was obtained in 75% yield. In fact compound **5** is resistant to oxidation in contrast to compound **4** which is readily converted to 3-cyanodiphenyltetrazolium chloride **16** by the action of t-butyl hypochlorite. This fact can be rationalized by the increased intramolecular hydrogen bonding due to the o-methoxy groups in compound **5**. Similar, treatment of **6** with **3a** lead to the isolation of the unrearranged triazolium salt **9a** which is relatively stable at low temperature. However, compound **9a** was changed after two hours at room temperature in the NMR tube into a mixture of 50% with the isomeric rearrangement product **12a** as indicated by the ^1H NMR. Isolation of isomeric triazolium salts from other nitriles and the mechanism of these reactions were reported.[8]



4,7,10,13,16, Ar = Ph; 5,8,11,14,17, Ar = o-$MeOC_6H_4$; 6,9,12,15, Ar = p-$MeOC_6H_4$

a, R = R' = CH_3; b, R = CH_3, R' = Ph; c, R = R' = $(CH_2)_4$; d, R = R' = $(CH_2)_5$

Scheme 1



18 19a,d

Scheme 2

Similarly, addition of each of **4, 5** to a solution of **3b** in methylene chloride afforded the corresponding formazyltriazolium salts **10b, 11b** respectively. On the other hand, similar treatment of **6** with **3b** afforded mainly the dication **15b** together with **12b** as a minor product. The cycloaddition of the salts **3c,d** with the appropriate derivatives **4-6** gave the corresponding rearranged products **10c,d, 11c,d** and **12d**.

Attempts to prepare **13b** by reacting **16** with **3b** were unsuccessful. This is most probably due the insolubility of the starting tetrazolium salt **16** in the reaction medium where it was recovered completely unchanged. Also, the use of two molar equivalent of **3b** in this reaction did not lead to the formation of the expected dication **13b**. However, oxidation of **10b** with t-butyl hypochlorite led to the quantitative formation of the dication **13b**. On the other hand, the dimethoxy analog **11b** was completely recovered unchanged upon treatment with t-BuOCl under similar or more drastic conditions (higher temperature or with variable excess of the oxidizing agent). Also, other oxidizing agents (e.g. NBS or NCS) reported for the synthesis of tetrazolium salts could not affect the conversion of **11b** to **14b**. Similar attempts with **5** failed to produce **17**, which reflects the stability of the bis(o-methoxyphenyl)formazans most probably due to the stronger intramolecular hydrogen bonding in this derivative.

Finally, addition of the crown cyanoformazan **18** to each of the 2-aza-1-azoniaallene salts **3a,d** led to high yields of the triazolium crown-formazans **19a,b** respectively. Also, attempts to oxidize the latter to their corresponding tetrazolium-triazolium dications were unsuccessful.

EXPERIMENTAL

All melting points were uncorrected. All experiments were carried out with exclusion of moisture in solvents dried by standard methods. ^1H and ^{13}C NMR spectra (δ scale) were recorded with a Bruker WM-250 and AC-250 spectrometer. The starting materials **1a-d**[4,6,8], **2a-d**[4,6,8], **4-6**[9-10], **16**[11,12] and **18**[2] were prepared as reported.

5-Cyano-1,3-bis(2-methoxyphenyl)formazan (**5**): To a cold (0°C) stirred solution of NaOH (12.0 g, 0.3 mol) in aqueous ethanol (250 ml, 50%) was added cyanoacetic acid (4.25 g, 50 mmol) followed dropwise addition of o-methoxybenzenediazonium chloride [prepared by treating a solution of o-anisidine (13.5 g, 110 mmol) in HCl (36 ml, 36%) at -5°C with a solution of $NaNO_2$ (7.6 g in 20 ml of H_2O) with stirring]. After addition was complete the mixture was stirred at 0°C for 3 h, then at room temperature overnight. It was then acidified with acetic acid and the precipitate was collected, washed with water and crystallized from MeOH/acetone mixture (50%) to give 7.7 g (70%) of deep red crystals of **5** mp 140-2°C. ^1H NMR ($CDCl_3$): 4.0 (s, 6H, OCH_3), 7.0-7.8 (m, 8H, ArH's), 13.9 (1H, NH). (Found: C, 62.35; H, 5.10; N, 22.53. Calcd for $C_{16}H_{15}N_5O_2$ (MW = 309.3): C, 62.13; H, 4.89; N, 22.64%).

Reaction of the α-Chloroazo Compounds **2a-d** with the Cyanoformazans **4-6, 18**: A solution of $SbCl_5$ (0.6 g, 2 mmol) in CH_2Cl_2 (5 ml) was added dropwise with stirring to a cold (-60°C) solution of the appropriate α-chloroazo compound **2a-d** (2 mmol) in CH_2Cl_2 (15 ml) followed by the appropriate cyanoformazan **4-6** (2 mmol) in CH_2Cl_2 (10 ml). The mixture was then stirred at -60°C for 1 h, then at 0°C for 1 h, and finally at room temperature for 1h. Filtration afforded in most cases an analytically pure crystalline product. Alternatively, the solvent was removed and the residue was crystallized.

2,3-Dimethyl-5-(1,5-diphenylformazan-3-yl)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**10a**): From **2a** and **4** after evaporation of the solvent in vacuo recrystallization from CH_3CN gave deep red crystals of **10a**, yield 1.2 g (70%), mp 195°C (dec). ^1H NMR (CD_3CN): 2.83, 3.75 (CH_3), 7.39-7.54, 7.94 (m, 10H , s, 2H, Aryl), 15.71(NH); ^{13}C NMR (CD_3CN): 14.5, 35.2 (CH_3), 120.7, 128.4, 130.7, 131.0, 131.6, 131.9, 136.7, 141.3, 147.1, 156.3, 162.2 (Ar, C=N). (Found: C, 33.32; H, 2.38; N, 11.87. Calcd for $C_{23}H_{19}Cl_9N_7Sb$ (MW = 834.3): C, 33.11; H, 2.30; N, 11.75%).

5-(1,5-Diphenylformazan-3-yl)-3-methyl-2-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**10b**): From **2b** and **4** after evaporation of the solvent in vacuo recrystallization from $CHCl_3$ gave deep red crystals of **10b**, yield 1.1 g (62%), mp 200-2°C (dec). ^{1}H NMR (CD_3CN): 2.69 (CH_3), 7.39-7.76 (Aryl), 15.83(NH); ^{13}C NMR (CD_3CN): 15.0 (CH_3), 79.1 ($CHCl_3$), 120.8, 128.9, 129.2, 129.25, 130.7, 131.0, 131.1, 131.7, 134.9, 136.6, 140.8, 146.9, 156.7, 163.0 (Ar, C=N). (Found: C, 33.88; H, 2.18; N, 9.81. Calcd for $C_{28}H_{21}Cl_9N_7Sb.CHCl_3$ (MW = 1015.7): C, 34.29; H, 2.18; N, 9.65%).

5,6,7,8-Tetrahydro-2-(1,5-diphenylformazan-3-yl)-3-(2,4,6-trichlorophenyl)[1,2,4]triazolo[5,1-a]pyridinium Hexachloroantimonate (**10c**): From **2c** and **4** the product precipitated as an analytically pure deep red crystals of **10c**, yield 1.2 g (65%), mp 194-6°C (dec). ^{1}H NMR (D_6-DMSO): 2.1, 2.2, 3.3, 4.1 (CH_2), 5.9 (CH_2Cl_2), 7.5 (m, Ph), 8.4 (s, $C_6H_2Cl_3$), 15.0 (NH). (Found: C, 32.93; H, 2.41; N, 10.49. Calcd for $C_{25}H_{21}Cl_9N_7Sb.CH_2Cl_2$ (MW = 945.2): C, 33.04; H, 2.45; N, 10.37%).

6,7,8,9-Tetrahydro-2-(1,5-diphenylformazan-3-yl)-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]-azepinium Hexachloroantimonate (**10d**): From **2d** and **4** the precipitated product was recrystallized from CH_3CN to give deep red crystals of **10d**, which was dried at 80°C for 2 h., yield 1.25 g (65%), mp 196-8°C (dec). ^{1}H NMR (D_6-DMSO): 1.86-1.91, 3.43, 4.35 (CH_2), 7.42-7.73 (m, Ph), 8.34 (s, $C_6H_2Cl_3$), 15.0 (NH). (Found: C, 35.78; H, 2.71; N, 11.10. Calcd for $C_{26}H_{23}Cl_9N_7Sb$ (MW = 874.3): C, 35.72; H, 2.65; N, 11.21%).

5-[1,5-Bis(2-methoxyphenyl)formazan-3-yl]-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11a**): From **2a** and **5** the product precipitated as an analytically pure deep red crystals of **11a** was collected and dried at 80°C for 1 h., yield 1.35 g (75%), mp 190-2°C (dec). ^{1}H NMR (D_6-DMSO): 2.92, 3.91, 3.98 (CH_3), 7.02-7.40, 8.36 (m, s, Aryl), 15.45(NH); ^{13}C NMR (D_6-DMSO): 13.5, 34.1, 56.3 (CH_3), 112.8, 115.3, 120.9, 127.0, 130.4, 131.5, 131.9, 134.8, 134.9, 139.4, 152.5, 154.3, 160.9 (Ar, C=N). (Found: C, 33.23; H, 2.58; N, 10.92. Calcd for $C_{25}H_{23}Cl_9N_7O_2Sb$ (MW = 894.3): C, 33.58; H, 2.59; N, 10.96%).

5-[1,5-Bis(2-methoxyphenyl)formazan-3-yl]-3-methyl-2-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11b**): From **2b** and **5** after evaporation of the solvent in vacuo recrystallization from CH_3CN gave deep red crystals of **11b**, yield 1.1 g (55%), mp 200-2°C (dec). ^{1}H NMR (CD_3CN): 2.71, 3.99 (CH_3), 6.97-8.05 (Aryl), 15.61(NH); ^{13}C NMR (CD_3CN): 14.6, 56.7 (CH_3), 113.3, 116.0, 121.4, 128.2, 128.7, 130.4, 130.9, 132.1, 132.1, 132.4, 134.2, 135.4, 135.7, 139.8, 153.2, 155.6, 162.6 (Ar, C=N). (Found: C, 37.85; H, 2.47; N, 10.05. Calcd for $C_{30}H_{25}Cl_9N_7O_2Sb$ (MW = 956.4): C, 37.68; H, 2.63; N, 10.25%).

5,6,7,8-Tetrahydro-2-[1,5-bis(2-methoxyphenyl)formazan-3-yl]-3-(2,4,6-trichlorophenyl)-[1,2,4]triazolo[5,1-a]pyridinium Hexachloroantimonate (**11c**): From **2c** and **5** the product precipitated as an analytically pure deep red crystals of **11c**, yield 1.5 g (82%), mp 192-4°C (dec). ^{1}H NMR (D_6-DMSO): 2.1-2.17, 3.34, 4.06 (CH_2), 3.99 (CH_3), 7.99-7.5 (m, Ar), 8.38 (s, $C_6H_2Cl_3$), 15.45 (NH); ^{13}C NMR (D_6-DMSO): 17.6, 20.8, 24.0, 46.4 (CH_2), 56.3 (CH_3), 112.9, 115.2, 120.9, 126.8, 130.3, 131.5, 131.9, 134.78, 134.83, 139.3, 152.5, 154.3, 160.7 (Ar, C=N). (Found: C, 35.19; H, 2.77; N, 10.45. Calcd for $C_{27}H_{25}Cl_9N_7O_2Sb$ (MW = 920.4): C, 35.24; H, 2.74; N, 10.65%).

6,7,8,9-Tetrahydro-2-[1,5-bis(2-methoxyphenyl)formazan-3-yl]-3-(2,4,6-trichlorophenyl)-5H[1,2,4]triazolo-[5,1-a]azepinium Hexachloroantimonate(**11d**): From **2d** and **5** the product precipitated as an analytically pure deep red crystals of **11d**, which was dried at 80°C for 2 h., yield 1.7 g (90%), mp 182-4°C (dec). ^{1}H NMR (D_6-DMSO): 1.89-1.94, 3.46, 4.35 (CH_2), 3.98 (CH_3), 7.00-7.49 (m, Ar), 8.35 (s, $C_6H_2Cl_3$), 15.45 (NH); ^{13}C NMR (D_6-DMSO): 22.6, 25.7, 27.6, 28.3, 48.6 (CH_2), 56.3 (CH_3), 112.9, 115.4, 120.9, 126.7, 130.5, 131.5, 131.9, 134.8, 135.2, 139.6, 152.5, 154.1, 165.2 (Ar, C=N). (Found: C, 35.77; H, 3.00; N, 10.38. Calcd for $C_{28}H_{27}Cl_9N_7O_2Sb$ (MW = 934.4): C, 35.99; H, 2.91; N, 10.49%).

5-[1,5-Bis(4-methoxyphenyl)formazan-3-yl]-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3H-1,2,4-triazolium Hexachloroantimonate (**9a**): From **2a** and **6** the precipitated analytically pure deep red crystals of **9a** was

collected, yield 0.6 g (30%), mp 145-50°C [decompose and resolidify and remelt again at 210-12°C (dec.)]. ^{1}H NMR (D_6-DMSO): 1.78 (s, 6H, CH_3), 3.86 (s, 6H, OCH_3), 5.76 (s, 2H, CH_2Cl_2) 7.03, 7.55 (2d, 8H, $2C_6H_4$), 8.03 (s, 2H, C_6H_2), 11.77, 15.21 (2s, 1H, NH). (Found: C, 32.11; H, 2.75; N, 10.32. Calcd for $C_{25}H_{23}Cl_9N_7O_2Sb.CH_2Cl_2$ (MW = 979.3): C, 31.89; H 2.57; N, 10.01%). After 2 h. at room temperature (in NMR tube in D_6-DMSO) 50% of the isomeric product **12a** appeared which showed additional signals at: 2.57, 3.03, 3.81 (CH_3), 7.2, 7.6 (2d, C_6H_4), 8.11 (s, C_6H_2).

5-[1,5-Bis(4-methoxyphenyl)formazan-3-yl]-3-methyl-2-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**12b**) and 2,3-Bis(4-methoxyphenyl)-5-[3-methyl-2-phenyl-1-(2,4,6-trichlorophenyl)-1-H-1,2,4-triazolium-5-yl]-2H-tetrazolium Bis(hexachloroantimonate (**15b**): From **2b** and **6** the precipitated analytically pure deep red crystals of **12b**, yield 0.4 g (20%), mp 190-2°C (dec). ^{1}H NMR (D_6-DMSO): 2.7, 3.85 (CH_3), 7.05, 7.48, 7.7, 7.8, 8.12 (d, 4H, d, 4H, m, 3H, d, 2H, s, 2H, Aryl), 15.34 (NH); ^{13}C NMR (D_6-DMSO): 14.2, 55.7 (CH_3), 114.8, 121.6, 127.6, 128.2, 129.8, 130.0, 139.4, 133.6, 135.1, 139.1, 139.7, 154.8, 160.6, 161.9 (Ar, C=N). (Found: C, 37.60; H, 2.35; N, 10.13. Calcd for $C_{30}H_{25}Cl_9N_7O_2Sb$ (MW = 956.4): C, 37.68; H, 2.63; N, 10.25%).
The mother liquor after evaporation was purified by dissolving in CH_3CN and reprecipitated by addition of ether to give yellow product of **15b**, 0.65 g (25%), mp 213-15°C (dec).^{1}H NMR (CD_3CN): 2.91, 3.91 (CH_3), 7.13-7.84 (Aryl); ^{13}C NMR (CD_3CN): 15.9, 57.3 (CH_3), 117.1, 124.7, 125.6, 128.3, 128.5, 128.6, 131.5, 132.3, 135.8, 136.9, 143.4, 146.2, 152.2, 165.5, 165.9 (Ar, C=N). (Found: C, 28.10; H, 2.14; N, 7.81. Calcd for $C_{30}H_{24}Cl_{15}N_7O_2Sb_2$ (MW = 1289.9): C, 27.94; H, 1.88; N, 7.60%).

6,7,8,9-Tetrahydro-2-[1,5-bis(4-methoxyphenyl)formazan-3-yl]-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo-[5,1-a]azepinium Hexachloroantimonate(**12d**): From **2d** and **6** the product precipitated as an analytically pure deep red crystals of **12d**, which was dried at 80°C for 2 h., yield 1.7 g (90%), mp 165-7°C (dec). ^{1}H NMR (D_6-DMSO): 1.85-1.94, 2.47-2.53, 4.3 (CH_2), 3.83 (OCH_3), 7.05, 7.47 (2d, Ar), 8.35 (s, $C_6H_2Cl_3$), 15.22 (NH). (Found: C, 35.75; H, 2.75; N, 10.20. Calcd for $C_{28}H_{27}Cl_9N_7O_2Sb$ (MW = 934.4): C, 35.99; H, 2.91; N, 10.49%).

5-{16,17-Dihydro-5H,15H-dibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecin-7-yl}-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**19a**): From **2a** and **18** the precipitated analytically pure deep red crystals of **19a** was collected, yield 1.6 g (90%), mp 215-7°C (dec). ^{1}H NMR (D_6-DMSO): 2.34, 4.42 (CH_2), 2.91, 3.91 (CH_3), 5.75 (CH_2Cl_2), 6.99-7.47 (m, 8H), 8.38 (s, 2H) (Aryl), 16.04 (NH); ^{13}C NMR (D_6-DMSO): 13.5, 34.0 (CH_3), 28.8, 68.1 (CH_2), 112.8, 114.3, 120.8, 127.1, 130.4, 131.6, 132.1, 134.1, 135.0, 139.4, 151.9, 154.2, 160.9 (Ar, C=N). (Found: C, 32.94; H, 2.66; N, 9.97. Calcd for $C_{26}H_{23}Cl_9N_7O_2Sb.CH_2Cl_2$ (MW = 991.3): C, 32.72; H, 2.54; N, 9.89%).

6,7,8,9-Tetrahydro-2-{16,17-dihydro-5H,15H-dibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecin-7-yl}-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate (**19d**): From **2d** and **18** the product precipitated in an analytically pure deep red crystals of **19d**, which was dried at 80°C for 2 h., yield 1.4 g (83%), mp 192-4°C (dec). ^{1}H NMR (D_6-DMSO): 1.9, 2.26, 3.4, 4.4 (m, CH_2), 7.0-7.40 (m, Ar), 8.41 (s, $C_6H_2Cl_3$), 16.06 (NH); ^{13}C NMR (D_6-DMSO): 22.6, 25.7, 27.5, 28.3, 28.8, 48.5, 68.1 (CH_2), 112.8, 114.4, 120.8, 126.7, 130.4, 131.6, 132.1, 134.1, 135.3, 139.6, 151.9, 154.1, 165.2 (Ar, C=N). (Found: C, 36.67; H, 2.99; N, 10.21. Calcd for $C_{29}H_{27}Cl_9N_7O_2Sb$ (MW = 946.4): C, 36.80; H, 2.88; N, 10.36%).

Reaction of t-BuOCl with the formazans **4**, **10b**: To a solution of the formazan (2 mmol) in $CHCl_3$ or CH_3CN (10 ml) at -10°C was added dropwise with stirring a solution of t-BuOCl (0.27 g, 2.5 mmol) in $CHCl_3$ (10 ml). The reaction mixture was further stirred at 5°C for 5 min. and the solvent was then removed under reduced pressure at 20°C. The remaining material was dissolved in $CHCl_3$ or CH_3CN and repriciptated by addition of dry ether.

5-Cyano-2,3-diphenyl-2H-tetrazolium Chloride (**16**): From **4** the product **16** was obtained as pale yellow powder 0.45 g (90%), mp 240-1°C (lit.[11] mp 139-40°C).

2,3-Diphenyl)-5-[3-methyl-2-phenyl-1-2,4,6-(trichlorophenyl)-1-H-1,2,4-triazolium-5-yl]-2H-tetrazolium Chloride Hexachloroantimonate (**13b**): From **10b** pale yellow powder of **13b** 1.8 g (97%), mp 245-7°C (dec). ^{1}H NMR (D_6-DMSO): 2.95 (s, CH_3), 7.6-7.94 (m, Ar), ^{13}C NMR (D_6-DMSO): 15.5 (CH_3), 124.6, 127.3, 128.3, 128.6, 131.0, 131.3, 131.7, 133.6, 135.3, 135.7, 136.9, 142.6, 146.0, 152.5, 165.7 (Ar, C=N). (Found: C, 36.35; H, 2.36; N, 10.31. Calcd for $C_{28}H_{20}Cl_3N_7.SbCl_6^-Cl^-$ (MW = 930.8): C, 36.13; H, 2.17; N, 10.53%).

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REFERENCES

1. Ibrahim, Y. A.; Elwahy, A. H. M.; Abbas, A. A. *Tetrahedron* **1994**, *50*, 11489.
2. Attiyat, A. S.; Ibrahim, Y. A.; Christian, G. D. *Microchem. J.* **1988**, *37*, 114.
3. Attiyat, A. S.; Ibrahim, Y. A.; Christian, G. D. *Microchem. J.* **1988**, *37*, 122.
4. Wang, Q.; Amer, A.; Mohr, S.; Ertel, E.; Jochims, J. C. *Tetrahedron* **1993**, *49*, 9973.
5. Wang, Q.; Al-Talib, E.; Jochims, J. C. *Chem. Ber.* **1994**, *127*, 541.
6. Wang, Q.; Amer, A.; Troll, C; Fischer, H.; Jochims, J. C. *Chem. Ber.* **1993**, *126*, 2519.
7. Wang, Q.; Mohr, S.; Jochims, J. C. *Chem. Ber.* **1994**, *127*, 947.
8. Wang, Q.; Jochims, J.C.; Kohlbrandt, S.; Dahlenburg, L.; Al-Talib, M.; Hamed, A.; Ismail, A. E. *Synthesis* **1992**, 710.
9. Shawali, A. S.; Abd El-Galil, M. *Tetrahedron* **1971**, *27*, 4305.
10. Wedeking, E. *Chem. Ber.* **1897**, *30*, 2993.
11. Iida, H; Manda, E. Tokyo Kogyo Shikensho Hokoku **1965**, *60*, 60; Kogyo Kagaku Zasshi *68*, 318 [*Chem. Abstr.* **1965**, *63*, 4424b].
12. Kuhlmann, U.; Severin, E.; Stellmach, J.; Wiezorek, C.; Echsler, K. *Acta Histochem. Suppl.* **1989**, *37*, 221; *Chem. Abstr.* **1989**, *111*, 190748.

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