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Reactions of Trimethylsilyl Cyanide with Tropone, 2-Phenyltropone, and 2-Methoxytropone. Formations of 2-Cyano-1-hydroxytropylidene Derivatives

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Reaction of trimethylsilyl cyanide (TMSCN) with tropone and 2-phenyltropone in the presence of a catalytic amount of zinc iodide in dichloromethane afforded silyl ethers of 7-cyano-1,3,5-cycloheptatriene-1-ol (**2a**) and 2-phenyl-7-cyano-1,3,5-cycloheptatriene-1-ol (**2b**), respectively. On the other hand, reaction of TMSCN with 2-methoxytropone gave 2-cyanotropone. Upon hydrolysis, **2a**, and **2b** yielded 2-cyano-1,3,5-cycloheptatrien-1-ol (**3a**) and a tautomeric mixture of 2-cyano-7-phenyl-1,3,5-cycloheptatrien-1-ol (**3b**) and 2-cyano-7-phenyl-3,5-cycloheptadien-1-one (**4b**). Oxidation of **3a** and the tautomeric mixture of **3b** and **4b** with selenium dioxide in dioxane afforded 2-cyanotropone and 2-cyano-7-phenyltropone, respectively.

Reactions of trimethylsilyl cyanide (TMSCN) with carbonyl compounds have attracted much attention from chemists because of their utility in the synthesis of cyanohydrin derivatives and of various compounds which can be derived from the cyanohydrins.[1] TMSCN is known to react with isolated and conjugated carbonyl groups to give 1,2-addition products[1a–e] and 1,4- or 1,6-addition products,[1f] respectively. Tropone derivatives are cyclic conjugated carbonyl compounds with aromaticity and their reactions with organometallic compounds such as Grignard reagents have attracted considerable attention from chemists,[2] however the reported examples of reactions of tropone derivatives with organosilane compounds are relatively few in number.[3] We reacted some tropone derivatives with TMSCN in the presence of a catalytic amount of zinc iodide. Here, we wish to report the result of these reactions.

Results and Discussion

When tropone (**1a**) and 2-phenyltropone (**1b**) were allowed to react with TMSCN in anhydrous dichloromethane in the presence of a catalytic amount of zinc iodide at room temperature for 5 d, silyl ethers of 7-cyano-1,3,5-cycloheptatrien-1-ol (**2a**)

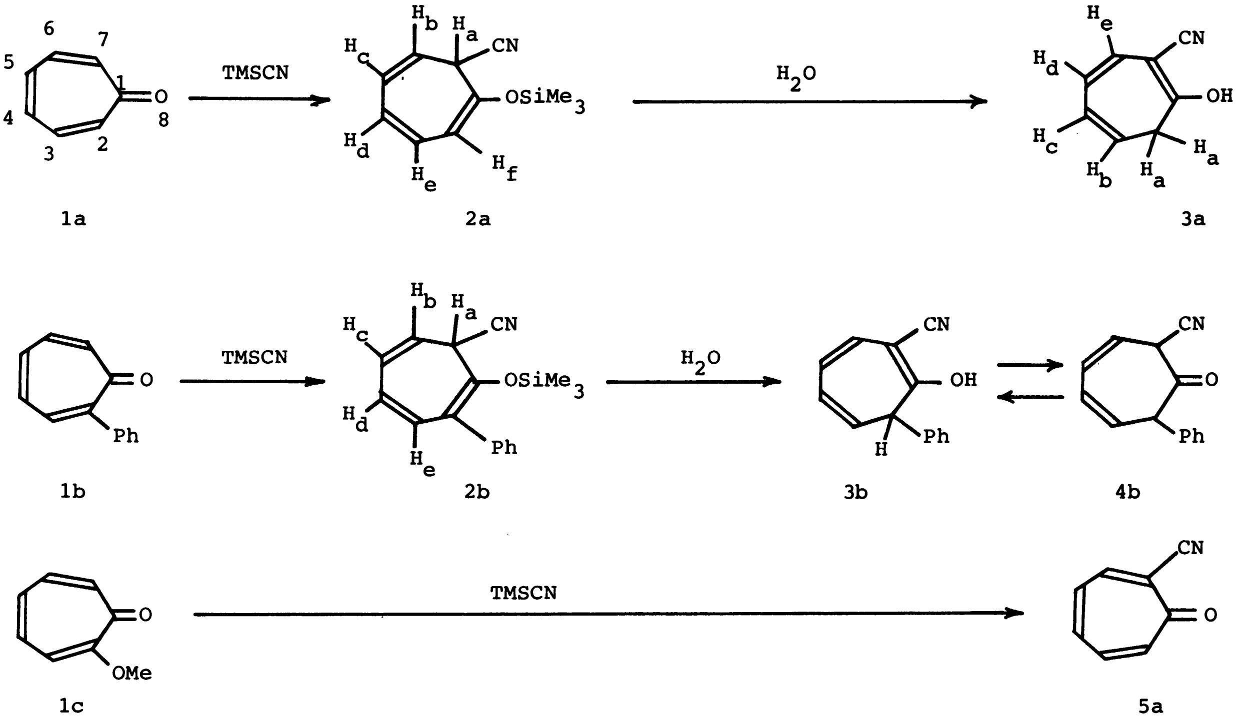

Fig. 1.

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and 2-phenyl-7-cyano-1,3,5-cycloheptatrien-1-ol (**2b**) were obtained in 54 and 59% yields, respectively. On the other hand, the reaction of TMSCN with 2-methoxytropone (**1c**) under the same conditions as above afforded 2-cyanotropone (**5a**) in 84% yield. Upon hydrolysis, **2a** and **2b** gave 2-cyanocycloheptatrien-1-ol (**3a**) and a tautomeric mixture of 2-cyano-7-phenyl-1,3,5-cycloheptatrien-1-ol (**3b**) and 2-cyano-7-phenyl-3,5-cycloheptadien-1-one (**4b**) in 84 and 93% yields, respectively. Oxidation of **3a** and the tautomeric mixture of **3b** and **4b** in dioxane with selenium dioxide afforded 2-cyanotropone (**5a**) and 2-cyano-7-phenyltropone (**5b**) in 54 and 67% yields, respectively.

The structures of **5a**[4a] and **5b**[4b] were confirmed by comparison of their physical properties with the literature values. The structures of the new compounds were deduced on the basis of their physical properties and confirmed by comparison of the physical properties to those of the analogous tropylidene derivatives.[5] The formation of **5a** and **5b** by the oxidation of **3a** and the tautomeric mixture of **3b** and **4b**, respectively, also supports the structures of **3a**, **3b**, and **4b**.

The reaction of **1a** and **1b** with TMSCN can be explained as shown in Fig. 3. The addition reaction of TMSCN to 2- and 8-positions of **1a** and to 7- and 8-positions of **1b** gives the corresponding silyl ethers **2**. It is known that nucleophilic reagents attack the carbon atom at the 2- or 7- position of the troponemoieties.[2] The hydrolysis of **2** affords 7-cyano-1,3,5-cycloheptatrien-1-ol derivatives (**6**), which tautomerize to the corresponding keto-forms **4**, which further tautomerize to **3**. The preferential formations of 1,3,5-cycloheptatrien-1-ol of the type **3** as opposed to the type **6** can be explained by the strong acidity of the methine proton attached to the carbon atom, which has the electron-withdrawing cyano group in **6** compared to that of the methine proton of **3**.

Two possible mechanisms may be considered for

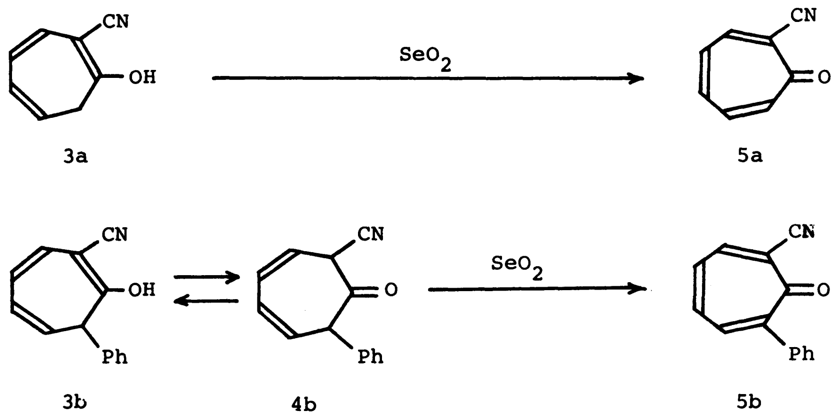

Fig. 2.

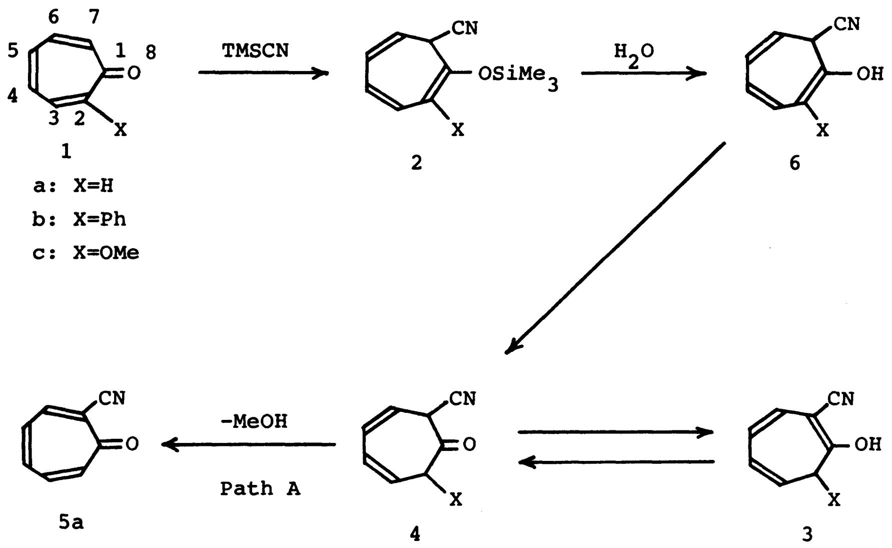

Fig. 3.

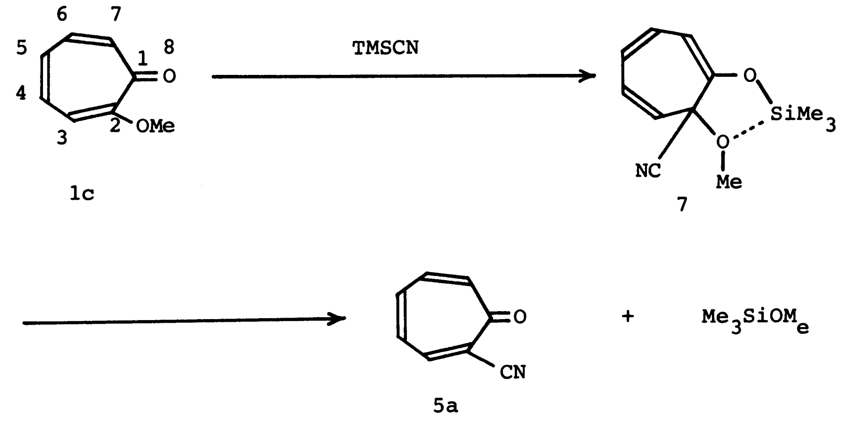

Fig. 4.

the formation of 2-cyanotropone (**5a**) by the reaction of TMSCN with 2-methoxytropone (**1c**). Pathway A involves 2-cyano-7-methoxycyclohepta-3,5-dien-1-one (**4c**) as an intermediate, which is formed through the same reaction path as that described above *via* the silyl ether derivative (**2c**) and the 1,3,5-cycloheptatrien-1-ol derivative (**6c**). Elimination of methanol from **4c** affords **5a**. Pathway B involves the intermediate **7**, which is formed *via* 2,8-addition of TMSCN to **1c**. Elimination of trimethylsilyl methoxide from the intermediate **7** leads to the formation of 2-cyanotropone (**5a**).* Pathway B does not need the existence of water for the formation of **5a**. The fact that despite the same anhydrous reaction conditions as those of the reactions of **1a** and **1b** with TMSCN, the silyl ether **2c** could not be detected seems to support pathway B.

Experimental

All the melting points are uncorrected. IR, UV, Mass, and high resolution Mass spectra were measured with DS-701G, Hitachi 220A, Hitachi M-52, and JMS-DX 300 spectrometers, respectively. NMR spectra were recorded with Hitachi R-20B spectrometer with tetramethylsilane as an internal standard. Wakogel C-200 and Wakogel B5F were used for column and thinlayer chromatography, respectively.

*Reaction of **1a** with TMSCN.* A mixture of **1a** (1.60 g, 15 mmol), TMSCN (2.97 g, 30 mmol), zinc iodide (100 mg), and anhydrous methylene chloride (20 ml) was stirred at room temperature for 5 d. After filtration, the solvent was evaporated on a rotary evaporator to yield a yellow oil, which was distilled under reduced pressure to yield a colorless oil of **2a** (690 mg, 54%, 0.2 Torr,† 85—90 °C).

2a: Found *m/z*: 205.09393. Calcd for $C_{11}H_{15}NOSi$: 205.09377. Mass *m/z* (rel intensity): 205 (M^+, 9), 190 (34), 131 (42), 103 (100). UV (EtOH): 280 nm (log ε, 3.49). IR (neat): 3030, 2960, 2240, 1620 cm^{-1}. NMR ($CDCl_3$) δ=0.3 (9H, s), 3.41 (H_a, d, J=7 Hz), 5.25 (H_b, dd, J=7 and 8 Hz), 5.7 (H_c, m), 6.2—6.6 (3H, m, H_d-H_f).

*Reaction of **1b** with TMSCN.* A mixture of **1b** (1.82 g, 10 mmol), TMSCN (1.98 g, 20 mmol), zinc iodide (100 mg), and anhydrous methylene chloride (20 ml) was stirred at room temperature for 5 d. After filtration, the solvent was removed on a rotary evaporator to yield a yellow oil, which was chromatographed on silica gel to yield a colorless oil of **2b** (1.65 g, 59%) by pet ether-benzene 1:1.

2b: Found *m/z*: 281.12362. Calcd for $C_{17}H_{19}NOSi$: 281.12362. Mass *m/z* (rel intensity): 281 (M^+, 57), 266 (100), 211 (60). UV (EtOH): 280 nm (log ε, 3.60). IR (neat): 3020, 2960, 2240, 1605 cm^{-1}. NMR ($CDCl_3$) δ=0.0 (9H, s), 4.05 (H_a, d, J=7 Hz), 5.57 (H_b, dd, J=7 and 8 Hz), 6.28 (H_c, m), 6.61 (2H, m, H_d, H_e), 7.3 (5H, m).

*Reaction of **1c** with TMSCN.* A mixture of **1c** (1.36 g, 10 mmol), TMSCN (1.98 g, 20 mmol), zinc iodide (100 mg), and anhydrous dichloromethane (20 ml) was stirred at room temperature for 5 d. The usual treatment of the reaction mixture gave a yellow oil, which was chromatographed on silica gel to yield crystals of **5a** (1.10 g, 84%, mp 139—140 °C, lit,[4a] 138—139 °C) by benzene-ether 1:1.

*Hydrolysis of **2a**.* A mixture of **2a** (410 mg, 2 mmol), water (1 ml), and dioxane (5 ml) was stirred at room temperature for 20h. The reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to yield a colorless crystals of **3a** (220 mg, 83%). Recrystallization from chloroform gave pure crystals of **3a**.

3a: Mp 127—128 °C. Found *m/z*: 133.04879. Calcd for C_8H_7NO: 133.04916. Mass *m/z* (rel intensity): 133 (M^+, 100), 115 (6), 104 (56). UV (EtOH): 283 nm (log ε, 3.67). IR (KBr): 3100, 2220, 1610 cm^{-1}. NMR ($CDCl_3$) δ=2.65 (2H, H_a, d, J=7 Hz), 5.40 (H_b, ddd, J=2, 7, and 8 Hz), 6.10 (H_c, m), 6.28 (2H, m, H_d, H_e), 6.50 (1H, bs, OH).

*Hydrolysis of **2b**.* A mixture of **2b** (850 mg, 3 mmol), water (5 ml), and dioxane (10 ml) was stirred at room temperature for 20h. The reaction mixture was extracted with ether, and dried over anhydrous sodium sulfate. After

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* The pathway B was suggested by a referee. We are indebted to the referee for this suggestion.

†1 Torr≈133.322 Pa.

filtration, the solvent was removed on a rotary evaporator to yield a yellow oil, which was chromatographed on silica gel to give a colorless oil of the tautomeric mixture of **3b** and **4b** (590 mg, 93%).

Tautomeric mixture of **3b** and **4b**: Found m/z: 209.08268. Calcd for $C_{14}H_{11}NO$: 209.08281. Mass m/z (rel intensity): 209 (95), 208 (42), 181 (96), 180 (100). UV (EtOH): 245 nm (log ε, 3.88). IR (neat): 3360, 3040, 2240 2220, 1723, 1600 cm^{-1}. NMR ($CDCl_3$) δ=2.69 (d, J=8 Hz), 3.31 (d, J=7 Hz), 4.35 (bs, OH), 5.8—6.5 (m), 6.9—7.5 (m).

Oxidation of 3a. A mixture of **3a** (265 mg, 2 mmol), selenium dioxide (270 mg, 2.4 mmol), and dioxane (5 ml) was refluxed for 30 min. After filtration, the solvent was removed on a rotary evaporator to yield a black tarry material, which was disolved in ethyl acetate, washed with aqueous saturated sodium hydrogencarbonate and water, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to yield a brown solid, which was thin-layer chromatographed on silica gel using benzene–ether 1:1 as a developing solvent to give crystals of **5a** (R_f=0.45, 125 mg, 54%).

Oxidation of the Tautomeric Mixture of 3b and 4b. A mixture of the tautomeric mixture of **3b** and **4b** (315 mg, 1.5 mmol), selenium dioxide (200 mg, 1.8 mmol), and dioxane (10 ml) was refluxed for 40 min. The reaction mixture was treated as usual to give a black tarry material, which was thin-layer chromatographed on silica gel using benzene–ether 8:2 as a developing solvent to give crystals of **5b** (R_f=0.40, 210 mg, 67%, mp 134—135 °C, lit,[4b] 134—135 °C).

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