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CHEMISTRY OF A MEISENHEIMER-TYPE σ-ADDUCT DERIVED FROM A TROPONOID

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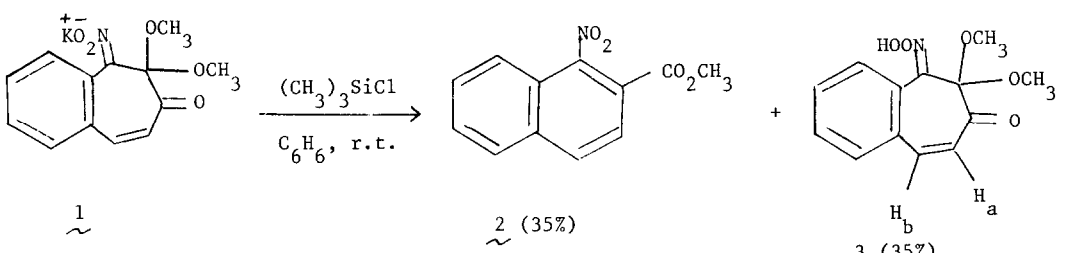
Summary - The gem-dimethoxy σ-adduct of methoxide addition to 2-methoxy-3-nitro-4,5-benzotropone reacts with either $(C_2H_5)_3OBF_4$, to change the nitronate into an oxime function, or $(CH_3)_3SiCl$, to give 2-carbomethoxy-1-nitronaphthalene and the nitronic acid corresponding to the starting adduct.

Interest towards Meisenheimer-type σ-adducts[1] has covered such various aspects as analytical[2] and technical[3] applications, the role as intermediates in nucleophilic aromatic substitution,[4] the detailed structure, particularly by n.m.r. techniques,[5] presumed biological roles,[6] and chemical transformations,[7] besides a continuous search for novel structures.[8]

Chemical transformations have so far only concerned σ-adducts derived from benzenoids.[7] However, we want to show here, taking as an example a σ-adduct derived from a troponoid, that also other classes of σ-adducts can be chemically modified. Thus, when an orange-coloured suspension of the σ-adduct 1[8a] (0.15 g; 0.51 mmol) in 10 ml of dried benzene was added of 0.17 ml (1.35 mmol) of $(CH_3)_3SiCl$ at room temperature, the colour rapidly faded. The solvent was evaporated in vacuo, the residue was taken with chloroform, KCl was filtered out and the



1 2 (35%) 3 (35%)

residue was chromatographed on a silica gel layer, eluant petroleum ether ethyl ether 1:1.

The R_F 0.58 band gave 2 (0.0406 g, 35%) as colourless needles (mp 147° from ethanol).

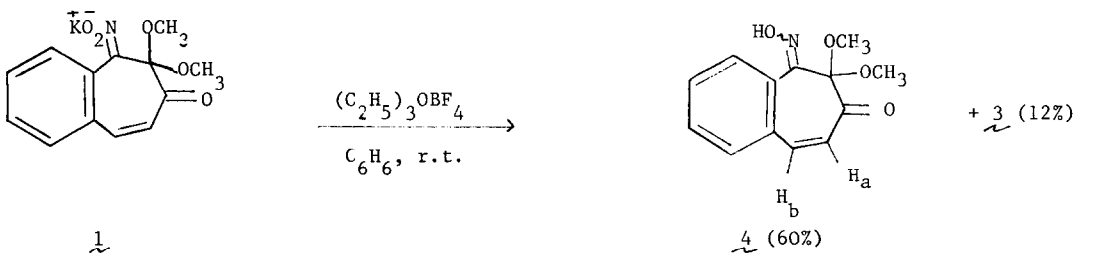
The R_F 0.25 band gave 0.0461 g (35%) of a colourless viscous oil, unchanged after repeated chromatography, to which we assign the nitronic acid structure 3 on the following basis. The ^{1}H NMR spectrum at room temperature shows absorptions at $\delta_{TMS}(CDCl_3)$ 3.3 (s, 3H OCH_3), 3.7 (s, 3H, OCH_3), 6.0 (s,1H, OH), 6.2 (d, J = 13 Hz, 1H, H_a), 7.1 (d, J = 13 Hz, 1H, H_b), and 7.6 ppm (m, 4H, aromatic protons). The IR spectrum (liquid film) shows absorptions at both 3400 and 1690-1680 cm^{-1} for the nitronic acid group. Finally, the UV spectrum ($(CH_3)_2SO$) shows λ_{max} at 315 nm. On addition of a drop of triethylamine to the mixture the absorption maximum was shifted to 475 nm, the spectrum being then identical to that of 1. [8a] The structural assignment was confirmed by the isolation of 3 in high yield from the treatment of 1 with 1 eq. of trifluoroacetic acid in benzene.

It is to be noticed from the above ^{1}H NMR data that the diastereotopic relationship between the methoxyl groups in 1 [8a] is retained in the conjugated acid 3.

When the reaction of 1 (0.79 mmol) with $(CH_3)_3SiCl$ (2.13 mmol) was carried out in dried tetrahydrofurane (10 ml), the residue from solvent evaporation failed to give a positive test for nitronic acids. Solvent evaporation, followed by sublimation, gave only 2 in a 60% yield.

In another experiment, a suspension of 1 (0.232 g, 0.77 mmol) in 12 ml of dried C_6H_6 was added of $(C_2H_5)_3OBF_4$ (0.339 g, 2.1 mmol) dissolved in 1 ml of dried CH_2Cl_2 whereby the orange colour due to 1 immediately faded to leave a pale-yellow solution, while KCl precipitated out. The mixture was filtered, evaporated in vacuo, and the solid residue was dissolved in CH_2Cl_2. On addition of petroleum ether, pale-yellow crystals precipitated out (0.114 g, 60%, mp 186° after sublimation at 150°, 0.2 mm), whilst from the mother liquor 3 was isolated (12%) by the technique described above.

To the mp 186° crystals, which analyzed correctly for $C_{13}H_{13}NO_3$, we assign structure 4 as a mixture of syn and anti oximes, on the following basis. The ^{1}H NMR spectrum shows



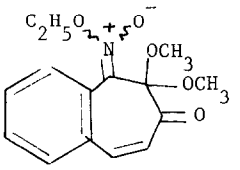
1

4 (60%)

absorptions at $\delta_{TMS}(CDCl_3)$ 3.4 (s, 6H, OCH_3), 6.06 (d, $\underline{J}$ = 13 Hz , 6.10 (d, $\underline{J}$ = 13 Hz), 7.12 (d, $\underline{J}$ = 13 Hz), 7.20 (d, $\underline{J}$ = 13 Hz), 7.5 (m, 4H, aromatic protons), and 10.4 ppm (broad s, 1H, OH). The 6.07 and 6.10 ppm doublets integrate together for 1H, and the same is true for the 7.12 and 7.20 doublets together. Double irradiations revealed the interdependence 6.06-7.12 and 6.10-7.20 between the doublets (on irradiation on a doublet the corresponding doublet became a singlet). The IR spectrum (nujol) shows absorptions at 3330, 1690 and 1680 for the oxime group.

As regards the reaction courses, hydrolysis of either $(C_2H_5)_3OBF_4$ or $(CH_3)_3SiCl$ by moisture (difficult to remove), followed by protonation of 1, obviously accounts for the formation of 3.

Moreover, the oximes 4 likely originate from ethylation of 1 to give the nitronic ester 5 (presumably as a syn-anti mixture), which decomposes into 4 and acetaldehyde. This pathway finds precedence in the picryl series.[10]



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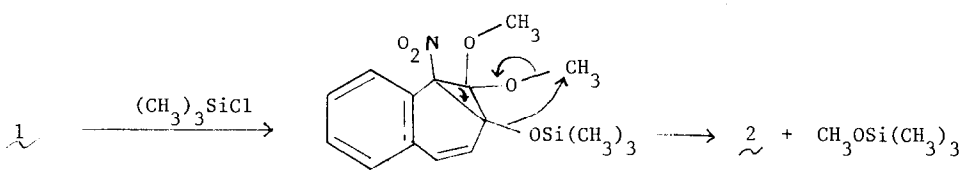
Finally, formation of 2 is more difficult to be rationalized. We propose the route of Scheme 1 wereby loss of a strongly basic silanolate is avoided by the concerted removal as a siloxane. Whereas troponoidal ring contraction to aromatic carboxylic acids, probably via



SCHEME 1

norcaradiene forms, is a common reaction for troponoids in alkali, [11] the process of Scheme 1 to give a carboxylic acid ester is, to the best of our knowledge, unprecedented.

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