Further Studies of the Interaction of Carbonyl Compounds with Organometallic Azides, the Reaction of Napthoquinones with Trimethylsilyl Azide

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Abstract:

1,4-Napthoquinone (1) and 1,2 Napthoquinone (6) on reaction with trimethylsilyl azide gave complex mixtures, with 2-amino-1,4-napthoquinone (5) and 4-amino-1,2-napthoquinone (10) being the major isolatable products. The mechanism is believed to involve conjugate 1,4 addition of trimethylslyl azide to an α,β-unsaturated carbonyl carbon, giving intermediate trimethylsiloxy azide adducts (2) and (7). Loss of nitrogen gives imine intermediates (4) and (8). Hydrolysis and tautomerization give amino napthoquinones (5) and (10). See plates 1 and 2. The mechanism is supported by the isolation of adduct (2a), the adduct of intermediate (2) with 1,4-napthoquinone. Anthraquinone fails to react, also consistent with this mechanism, as 1,4 addition of trimethylsilyl azide would disrupt the aromaticity of one ring.

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Discussion:

It was thought that quinones would react with trimethylsilyl azide by a 2+3-cycloaddition giving a triazoline product. Previously we reported (Ref 1) that benzoquinone in warm non polar solvents instead gave a complex mixture of products, primarily 2,5-diazido benzoquinone, 1,4-BIS-trimethylsiloxy)benzene, and "quinhydrone", the 1:1 adduct of hydroquinone, and quinone . For 1,4-napthoquinone (1) and 1,2 Napthoquinone (6), neither 2+3-cycloaddition nor the benzoquinone sequence occurred. No azido napthoquinones or quinhydrone analogs were detected, but 2-amino-1,4-napthoquionone (5) and 4-amino-1,2-napthoquinone (10) were instead the major isolatable products. Much intractable material was present under all reaction conditions. The reaction times also were substantially longer than for 1,4-benzoqinone. The mechanism is believed to involve conjugate 1,4 addition of trimethylslyl azide to an α,β unsaturated carbonyl carbon, giving intermediate trimethylsiloxy azide adducts (2) and (7), which on loss of nitrogen give imine intermediates (4) and (8). Hydrolysis and tautomerization give amino napthoquinones (5) and (10). The mechanism is supported by the isolation of dimer (2a), the adduct of (2) with 1,4-napthoquinone. Anthraquinone fails to react, also consistent with this mechanism, as conjugate 1,4 addition of trimethylsilyl azide would disrupt the aromaticity of one ring. The proposed mechanistic sequence is summarized on Plates 1 and 2. These reactions have only limited synthetic utility due to only fair yields of amino napthoquinones and long reaction times.

PLATE 1

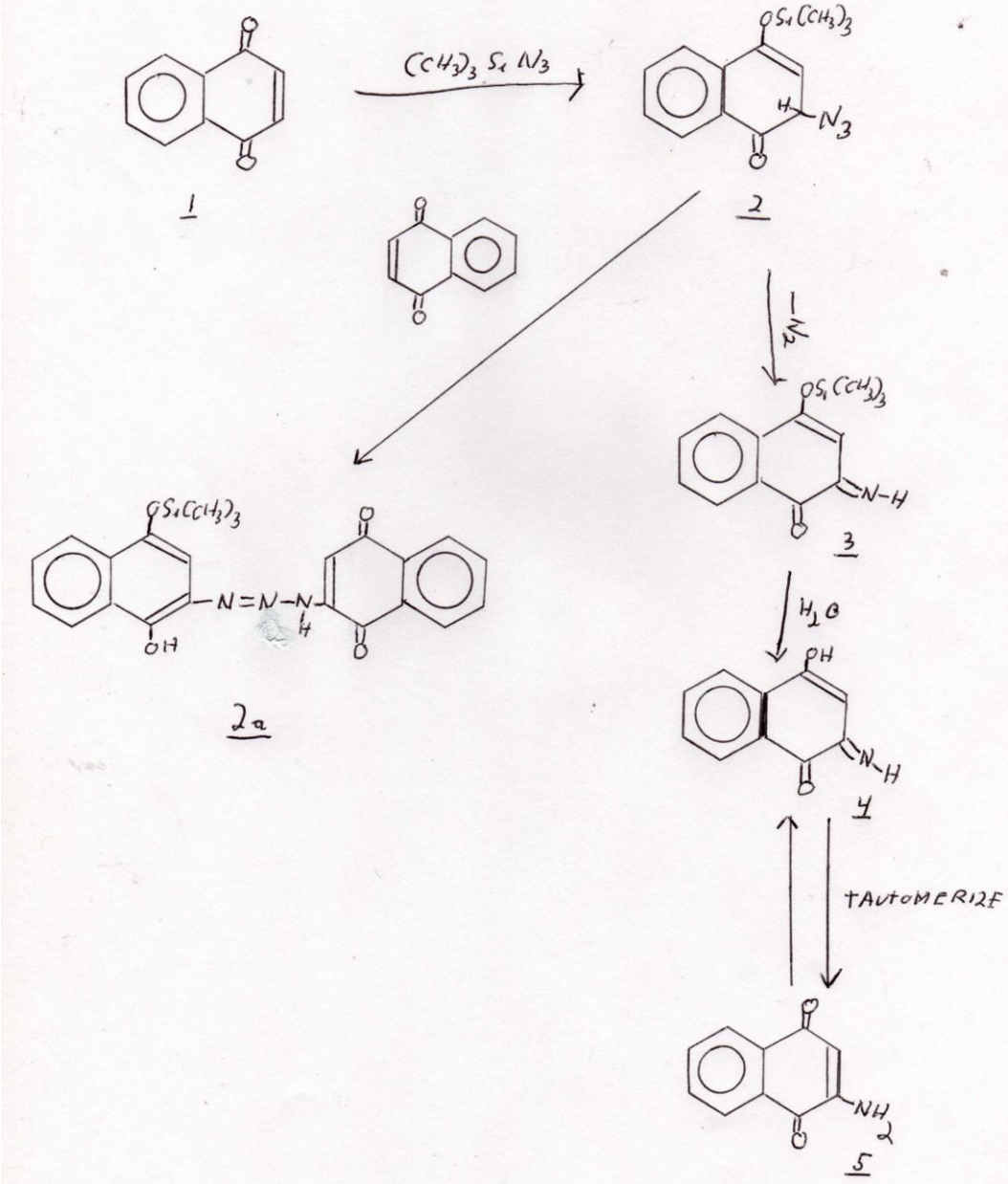
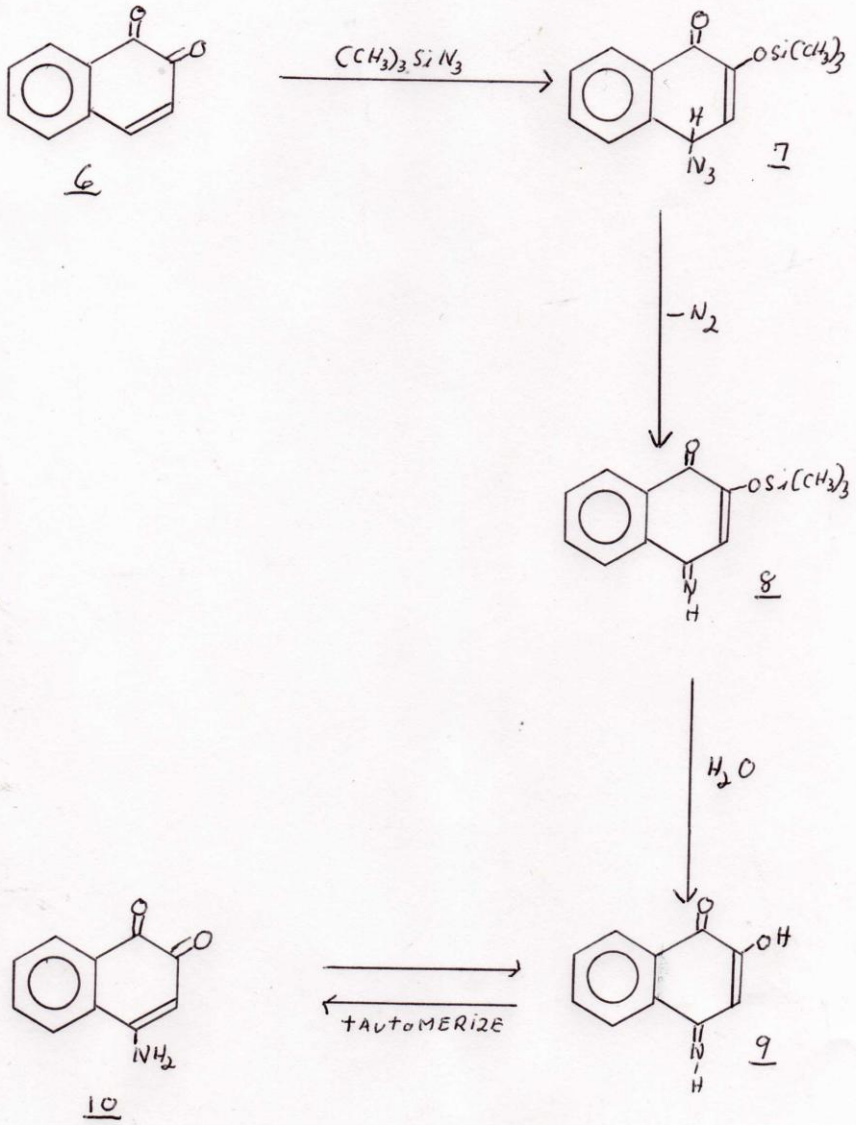


PLATE 2


(CH3)3SiN3
OSi(CH3)3
H
N3
6
7
-N2
OSi(CH3)3
N
H
8
H2O
NH2
10
TAUTOMERIZE
OH
N
H
9

Experimental:

Reaction of 1,4-Napthoquinone (1) with Trimethylsilyl Azide

To a 100 ml 3 neck round bottom flask was charged 6.4 g (0.040 mol) resublimed 1,4-napthoquinone, with stirring, in 100 ml toluene. The homogeneous solution was heated to 100° and charged with 5.8 g (0.050 mol) trimethylsilyl azide. Heating was continued under nitrogen and the mixture periodically analyzed by TLC (silica gel, toluene eluent). After ~ 24 hr reflux TLC showed 2 new spots and only a trace of napthoquinone. The mixture was cooled, and a yellow solid (2a), identified as the adduct of intermediate (2) with 1,4-napthoquinone, (2a), precipitated from the solution. Wt 1.5 g. Recrystallization from benzene gave yellow crystals, (2a), m.p, 238-41°.
I.R. (nujol), 3400 (broad, OH, 1680, congugated C=O, 1590 (aromatic), 1050 (trimethylsiloxy), cm^{-1}.
UV (extinction coefficient) (methanol), 228(11,000), 248(9000), 285(8000), 298(7200), 395 (1300) mu.
Mass Spec m/e 431 (parent ion).
PMR (100Mhz, $CDCl_3$), δ 7.4 (12H, aromatics +OH + N-H), 0.37 (9H, trimethylsiloxy).
A Hinsburg test was performed on 2a, by reaction with p-toluenesulfonyl chloride. The amide adduct was insoluble in dilute NaOH and HCl, indicative of a secondary amine, and consistent with the proposed structure.
Anal. Calc. For $C_{23}H_{21}N_3O_4Si$:

C, 64.02, H, 4.91, N, 9.74.

Found: C, 64.08, H, 4.55, N, 9.58. Satisfactory.

The mother liquor from above was concentrated on the rotovap, and chromatographed on a 1.5 x 2 inch column with benzene eluent. Nine fractions containing solid material were obtained. They were combined and sublimed at 150° with pump vacuum (0.1mm). 1.4g (20%), 2-amino-1,4-napthoquinone (5) was collected on the cold finger. Recrystallization from acetone gave orange crystals, m.p. 203°, (lit: [2], m.p. 206°).

I.R. (nujol), 3200 (broad, OH, 1680, congugated C=O, 1620 (aromatic), 1550, 1280,990,840,780,730 cm^{-1}.

PMR (100Mhz, DMSO), δ 7.68(m, aromatics). 5.7 (s, 1H, olefinic), 6.85(s, broad, NH_2).

Anal. Calc. For $C_{10}H_7NO_2$:

C, 69.40, H, 4.04, N, 8.10.

Found: C, 69.11, H, 3.76, N, 7.82. Satisfactory.

Reaction of 1,2-Napthoquinone (6) with Trimethylsilyl Azide

To a 50 ml 3 neck round bottom flask was charged 0.6 g (0.0038 mol) resublimed 1,2-napthoquinone with stirring in 25 ml benzene. The deep red solution was heated to 80° and charged with 1 ml (excess) trimethylsilyl azide. Heating was continued under nitrogen at 80° and the mixture periodically analyzed by TLC (silica gel, benzene eluent). After ~ 24 hr reflux TLC showed a new spot and only a trace of napthoquinone. A red precipitate was formed which was suction filtered from the mother liquor. Solvent was rotovaped from the mother liquor and the combined solids sublimed (180°, 0.33mm), yielding 0.55g (67%)

4-amino-1,2-napthoquinone (10), m.p. 270° (color change), (lit:[3], m.p. 270 °, color change).

I.R. (nujol), 1686(congugated C=O).

PMR (100Mhz, DMSO), δ 7.80(m, 6H,aromatics, + =N-H and OH). 5.64 (d, J= 2.5 Hz, 1H, olefinic). In DMSO the compound exists as tautomer (9). This form has precedence in the literature for basic solutions (ref: [4]).

References:

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4) **L.F. Fieser and M. Fieser, J. Amer. Chem. Soc., 56, 1565 (1934).**