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[2+2]- and [3+2]- Cycloadditions of Allylsilane to Quinones: Divergence from the Sakurai Reaction

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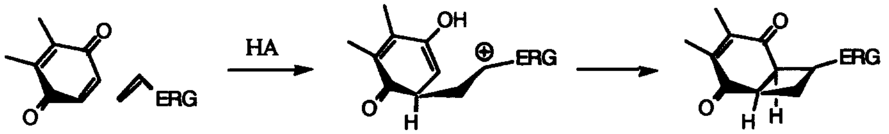
Abstract: Naphthoquinone **1** reacts with allyltrimethylsilane in the presence of Me_2AlCl at 78°C to yield a mixture of the [2+2]- and [2+3]- cycloadducts, **2** and **3**.When the cyclobutane **2** was treated with Me_2AlCl it rearranged stereospecifically to the cyclopentane **3**. © 1997 Elsevier Science Ltd.

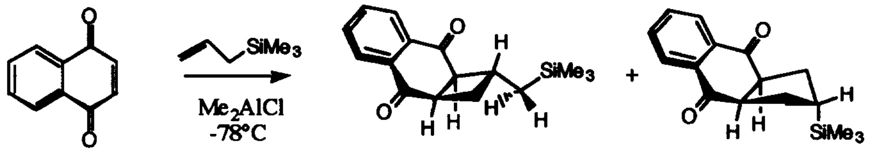
We have investigated the annulation of enaminoesters,[1] enaminoketones,[2] benzyl diethylmalonates,[3] styrenes,[4] dihydrofurans and dihydropyrans[5] to quinones. We noted that alkenes when appropriately substituted will undergo Lewis acid promoted two-step [2+2]-cycloaddition. A substituent capable of stabilising a carbocationic site, such as an electron releasing group, fulfills this requirement (Scheme 1).



Scheme 1

We have extended our work to an investigation of the reactions± of allyltrimethylsilanes with quinones in the presence of Lewis acids. We now report our preliminary results. We had earlier observed[4] that the soft Lewis acid Me_2AlCl[6] was highly effective at promoting electrophilic addition reactions of alkenes and again employed it in this system, at low temperature (-78°C). After ten minutes the reaction was rapidly quenched (aq $NaHCO_3$). The two products the [2+2] - cycloadduct **2**[11] and the [2+3] - cycloadduct **3**[13] were isolated in 34% and 23% yield, respectively. Naphthoquinone (**1**, 20%) was also recovered. There were no other products. This reaction pathway has not been observed previously and contrasts dramatically with that of the Sakurai reaction in which quinones react with allylsilanes in the presence of $TiCl_4$ to yield allylquinones.[7]

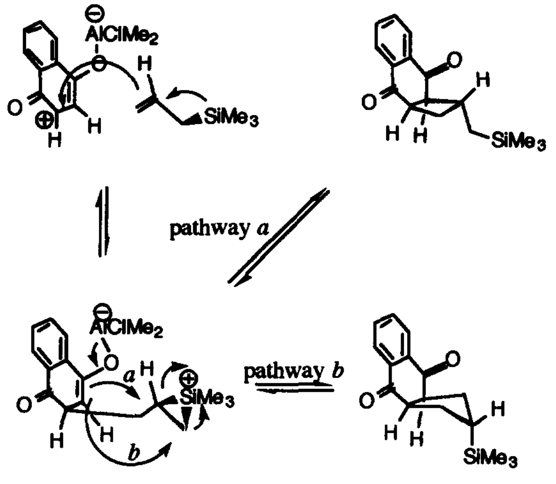
The structural relationship of the two products suggested to us that the cyclobutane **2** may have been the product of kinetic control and the cyclopentane **3** that of thermodynamic control. The cyclobutane **2** was therefore treated with Me_2AlCl at -78°C. Rearrangement did occur, slowly.



1 2 3

Scheme 2

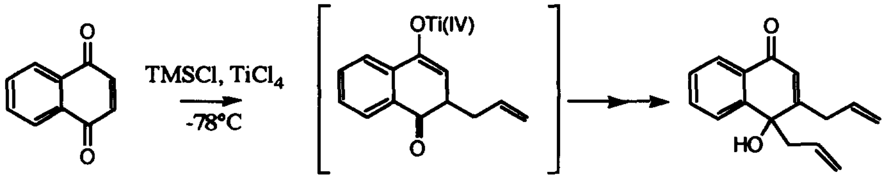
When the reaction was warmed to 0°C, the cyclopentane **3** was formed in essentially quantitative yield. A trace of 2-allylnaphthoquinone, the Sakurai product, was also detected. When the product **3** was treated with Me_2AlCl at -78°C and then warmed to 0°C, it was recovered unchanged. The rearrangement of **2** to **3** was stereospecific. No trace of a diastereomer of **3** was detected. On the basis of these results we propose the following mechanism (Scheme 3).



Scheme 3

We propose that the allylsilane orients itself in the transition state leading to the intermediate siliranium ion[8]such that the prochiral hydrogen subtends the quinone ring, for steric reasons. *Trans* involvement of the allyl π-bond in the silane follows, for reasons discussed earlier.[9] In this manner, the R'R' relative stereochemistry of the siliranium ion is controlled, whether it is formed directly from the quinone **1** or from the cyclobutane **2**. This accounts for the formation of only one cyclobutane steroisomer **2**, and retention of configuration during rearrangement to the product, **3**. Although this is the first time that the stereochemistry of this rearrangement has been proved in a carbocyclic system, Meyers[10] had earlier determined in a heterocyclic system, that a close analogue of this rearrangement occurs with retention of configuration.

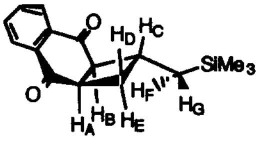
In view of these unexpected results, we investigated the reaction of naphthoquinone **1** and TMSCl using the Sakurai catalyst. Although this particular reaction had not been investigated previously,[6] our results (Scheme 4) mirror those of Sakurai[7] exactly, in that allylnaphthoquinone was the major product. The bis - adduct **5**[11] was also formed, presumably *via* the intermediate **4**. Trace amounts of the cycloadduct **3** were also isolated.



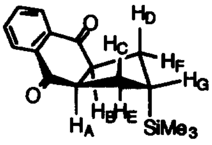
1 **4** **5**

Scheme 4

The structures **2** and **3** were established, by means of a range of spectroscopic methods which included ^{1}H,^{1}H COSY, ^{1}H decoupling and NOEDS. The broadband decoupled ^{13}C nmr spectrum and DEPT spectra of **2** were entirely consistent with this structure.[11] The ^{1}H nmr was considerably more complex.[11] The two diastereotopic geminal protons H_F and H_G appeared as two distinct double doublets. Although each possessed a geminal coupling constant, *J* 14.3Hz, both protons were unequally coupled to the neighbouring methine proton, H_C, *J* 4.4 and 11.1Hz. Connectivity was unequivocal on the basis of the ^{1}H,^{1}H COSY spectrum. However, ambiguity arose when it was observed that $J_{AB}=J_{BC}$, *i.e.* that $^3J_{cis}= {}^3J_{trans}$ in cyclobutanes as had been observed by others.[12] It transpired that the stereochemistry of the methylenetrimethylsilyl group relative to the bridgehead hydrogens could be interpreted as having either a *cis* or a *trans* configuration. The nOe difference experiments were investigated. The critical experiments were the following. Irradiation of H_B produced an nOe enhancement of H_F (3.9%) and H_G (2.3%):



2



3

In addition, irradiation of H_E resulted in an enhancement (1.9%) of H_B. Finally, irradiation of H_F resulted in the enhancement of both H_B and H_E. The enhancement of H_F was reciprocated when each of H_B and H_E was irradiated. The restricted conformation of **2** may be deduced from the coupling constants, J_{CF} and J_{CG}. The preferred orientation of the TMS group[10] is such that it eclipses H_C and thereby avoids awkward steric interactions with the bridgehead hydrogens.

The structure of **3** was similarly determined by means of ^{1}H,^{1}H COSY, ^{13}C, DEPT and ^{1}H,^{1}H decoupling experiments.[13] Again determination of the relative stereochemistry demanded nOe. The relative stereochemistry of the trimethylsilyl group could not be determined unambiguously from the ^{1}H nmr spectrum. The following two nOe experiments were decisive: irradiation of H_G resulted in the enhancement of H_D and H_C (5%) and irradiation of H_F in the enhancement of H_B and H_A(5%). The structure was unequivocally assigned as **3**.

Knölker[14] has investigated the application of the Sakurai reaction to enones and has concluded that [3+2]-annulation invariably accompanies allylation. Additionally, annulations claimed as [2+2] by others,[15] including Sakurai's group,[16] have been incorrectly assigned, according to him.[14] Our results point to another possible reaction pathway for the Sakurai reaction: that kinetic control leads to [2+2]- cycloaddition and thermodynamic control to [3+2]-cycloaddition.

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8. Both hyperconjugation (vertical stabilisation) and siliranium ion formation (non-vertical stabilisation) have been employed to explain β-carbocation stabilisation by silicon. We favour the latter since it is a more economical descriptor. Whilest silicon does not have electrons readily available for donation, one may envisage silicon involvement by 'pull' rather than 'push' (see: Lambert, J.B. *Tetrahedron*, **1990**, 46, 2677-2689).
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11. All new compounds had satisfactory microanlaysis. **2** : light orange, m.p.41-43° C ; ν_{max} / cm^{-1} (KBr) 2951(s), 2898 (m), 1681 (s), 1594 (s), 1289 (s), 1249 (s), 1128(m) and 839(s); δ_H (270MHz) 8.11-8.15 (2H,m,Ar*H*) , 7.73 - 7.80 (2H, m, Ar*H*), 3.44 (1H, ddd *J* =10.1, 7.6, 3.2 Hz), 3.29 (1H, dd, *J* =7.6, 7.6 Hz), 2.59-2.70 (1H,m), 2.45 (1H ddd, *J* =11.8, 7.6, 3.2 Hz), 2.28 (1H, ddd, *J* =11.8, 10.1, 9.1 Hz), 1.14(1H, dd,*J* =14.3,4.6 Hz), 0.89 (1H, dd, *J* =14.3,11.1Hz) and -0.05 (9H,s); δ_C (67.80 MHz) 200.0 (C), 196.7 (C), 136.6 (C), 136.3 (C), 135.4 (CH), 135.1 (CH), 128.4 (CH), 128.3 (CH), 55.3 (CH), 42.2 (CH), 40.6 (CH), 35.8 (CH_2), 26.3 (CH_2) and -0.10 (CH_3 x 3); LREIMS 272 (M^+,10%), 257 (3), 231 (38), 182 (8), 155 (5), 91 (10) and 73 (100).
12. See for example: Vogel, A. *Textbook of Practical Organic Chemistry* , **1989**, Fifth Edition, p.1423.
13. **3**: colourless oil; ν_{max} / cm^{-1} (film) 2923 (m), 1688 (s), 1594 (m),1289 (m), 1259 (s) and 836 (m); δ_H (270MHz) 8.05 -8.11 (2H, m, Ar*H*), 7.71 -7.77 (2H, m, Ar*H*) (3.29 -3.38 (2H, m), 2.33 (2H, ddd ,*J* = 17.3 , 9.7, 4.2 Hz), 1.85 (2H, ddd, *J* = 17.3, 9.7, 5.7Hz), 1.17 (1H, p,*J* =9.7Hz) and -0.05 (9H, s); δ_C (67.80Mz), 198.2 (C x 2), 134.8 (C x 2), 134.2 (CH x 2), 127.0 (CH x 2), 53.0 (CH x 2), 32.2 (CH x 2), 23.7 (CH) and -3.23 (CH_3 x 3).
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