Photocyclisation Between Allyltrimethylsilane and 1,4-Naphthoquinone and Ring Cleavage of the Resulting Cyclobutane Assisted by the Trimethylsilyl Group

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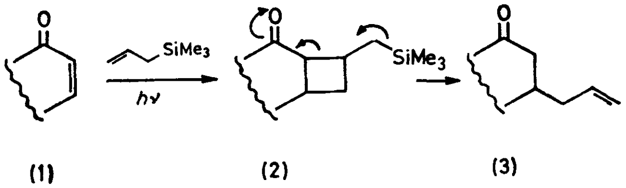
Summary Trimethylsilyl group-assisted opening of the cyclobutane ring of the product of the photochemical reaction of allyltrimethylsilane with 1,4-naphthoquinone followed by oxidation leads to the formation of allylnaphthoquinone.

Although there are numerous reports concerning reactions of allylsilanes, almost all are concerned with reactions with electrophiles.[1] Our interest in the chemistry of allylsilanes prompted us to study the cycloaddition of allylsilanes to photoactivated double bonds, *e.g.* (**1**), because ring opening of the product (**2**) assisted by the trimethylsilyl group in a stepwise or concerted manner would be expected to give the important allyl derivatives (**3**) as shown in Scheme 1.



Scheme 1

Irradiation† of a water-cooled solution of excess of the allylsilane (**4a**) and 1,4-naphthoquinone (**5**) in benzene led to a mixture of stereoisomers of the cyclisation product

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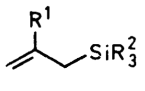
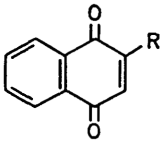
† Irradiations were performed on degassed solution using a high-pressure mercury lamp.

(**9**) in 69% yield. As expected, the cyclobutane ring of (**9**) was smoothly cleaved; on treatment with BF_3–Et_2O in dichloromethane at 0 °C followed by oxidation with aqueous $FeCl_3$, compound (**9**) gave the allylnaphthoquinone (**7**)[2] in 92% yield. Photocyclisation of the quinone (**5**) with the allylsilane (**4b**) followed by cleavage of the cyclobutane ring of the product and $FeCl_3$ oxidation afforded the allyl compound (**8**)[3] in 14% yield. Photocyclisation and cleavage between the quinone (**6**) and the allylsilane (**4a**) gave the product (**10**)‡ in 39% yield regioselectively.

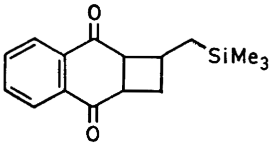


(4)

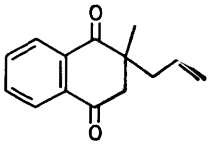
a; $R^1 = H, R^2 = Me$
b; $R^1 = R^2 = Me$
c; $R^1 = CH_2SiMe_3, R^2 = Me$
d; $R^1 = CH_2SiCl_3, R^2 = Cl$



(5) R = H
(6) R = Me
(7) $R = CH_2CH{=}CH_2$
(8) $R = CH_2C(Me){=}CH_2$

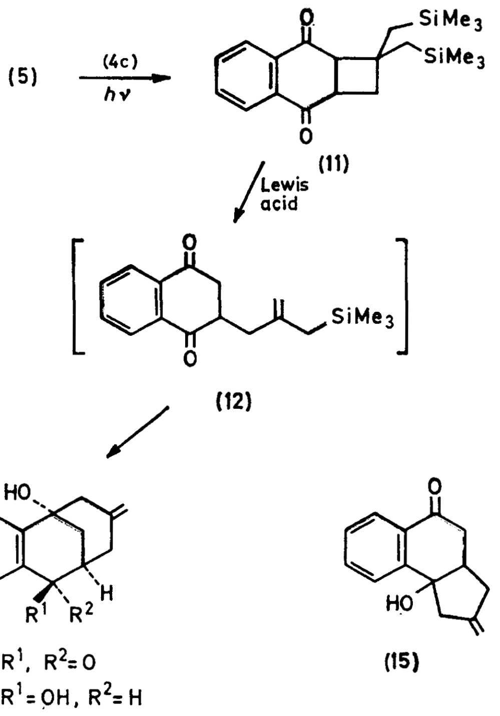


(9)



(10)

Subsequently we extended this reaction using the interesting allylsilane (**4c**). Condensation[4] of trichlorosilane with 3-chloro-2-chloromethylprop-1-ene in the presence of triethylamine and a catalytic amount of CuCl afforded the silane (**4d**), which on methylation with methylmagnesium bromide gave the desired allylsilane (**4c**) in 61% overall yield. Photocyclisation between (**4c**) and (**5**) afforded the cyclobutane (**11**) in 44% yield, which on treatment with BF_3–Et_2O or $SnCl_4$ in dichloromethane gave the tricyclic alcohol (**13**) in 28 or 32% yield, respectively, as a result of cleavage followed by cyclisation, probably *via* the intermediate (**12**) (Scheme 2).[5] Structure (**13**) was assigned on the basis of its ^1H n.m.r. spectra and spectra of the diol (**14**) derived through $NaBH_4$ reduction, which eliminated the alternative isomeric structure (**15**).



Scheme 2

(*Received*, 17*th February* 1981; *Com.* 181.)

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‡ Satisfactory analytical and spectral data have been obtained for all new compounds reported in this communication.

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[2] Y. Naruta, *J. Am. Chem. Soc.*, 1980, **102**, 3774.
[3] A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1977, 4041.
[4] *Cf.* D. Seyferth and R. E. Mammarella, *J. Organometal. Chem.*, 1978, **156**, 299; N. Furuya and T. Sukawa, *ibid.*, 1975, **96**, C1.
[5] *Cf.* B. M. Trost and J. E. Vincent, *J. Am. Chem. Soc.*, 1980, **102**, 5680.