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REACTIONS OF ALLYLSILANES WITH QUINONES. SYNTHESIS OF ALLYL-SUBSTITUTED HYDROQUINONES[1]

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Allyl-substituted hydroquinones have been prepared conveniently by the reaction of allylsilanes with various p-quinones in the presence of a Lewis acid in moderate yield. p-Allylquinols were also obtained regioselectively from 2, 6-disubstituted quinones.

Allylation of quinones[2-5] is an important reaction for preparing isoprenoid quinones[6-9] which play an important role in biological processes[10-12] such as electron transport, blood clotting, and oxidative phosphorylation. We wish to report herein a novel and convenient allylation of quinones with allylsilanes. Thus, in the course of studies on the further application of allylsilanes to organic synthesis,[13] it has been found that the reaction of allylsilanes with various quinones activated by a Lewis acid in dichloromethane produces the corresponding allyl-substituted hydroquinones and/or p-allylquinols in moderate yield. Although the type of the product depends upon the substrate employed, the reaction is quite general as shown in Table 1.

The reaction was carried out by the dropwise addition of an allylsilane (1 mmol) in dichloromethane (2 ml) to a quinone (1 mmol) in the presence of titanium tetrachloride (1 mmol) in dichloromethane (5 ml) under nitrogen at -78°C. After addition was complete, the reaction mixture was stirred at -78°C for a period indicated in the table. The mixture was hydrolyzed and the crude product was extracted by ether. The ethereal layer was dried over anhydrous sodium sulfate and concentrated, and then the crude product was purified by preparative thin layer chromatography on silica gel developing with a mixture of n-hexane, ether and/or ethyl acetate.

All p-quinones except for those having substituents on both 2- and 6-positions react to produce allyl-substituted hydroquinones, while 2, 6-disubstituted p-quinones studied produce p-allylquinols regioselectively[5] in moderate to high yield. A major side product in all reactions is the hydroquinone arizing from simple reduction of the substrate. The reaction should be carried out at low temperature to avoid the formation of complex products.

Although the mechanism of this allylation reaction has not yet been clarified, the results can be rationalized by Scheme 1, in which the initial p-allylquinol formation by 1,2-addition of the allylsilane to the quinone[14] takes place at low temperature. The resulting quinols, consecutively, may undergo allyl shifts via the [3,3] sigmatropic process as is seen in the related allylquinol rearrangement.[5] However both the presence of the dealkylation product from 2,5-di-t-butyl-1,4-benzoquinone (run 5) and the simultaneous formation of the p-allylquinol along with the allylnaphthoquinone from 2-methyl-1,4-naphthoquinone under the reaction condition (run 7),[15] strongly suggest that the another likely mechanism involving the dienone-phenol rearrangement by acid catalysis[16] cannot be dismissed at this time. The present reaction rather resembles to the p-allylquinol rearrangement catalyzed by boron trifluoride.[6] Related works are on progress.

Scheme 1

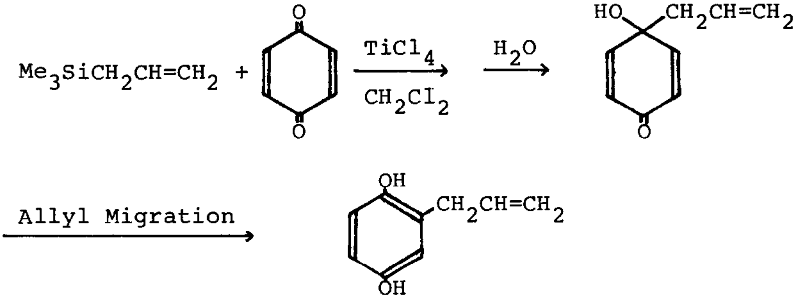

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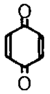
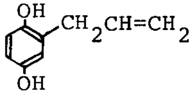
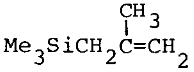
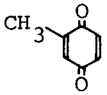
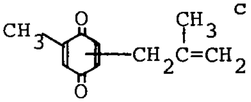
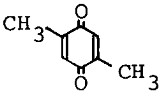
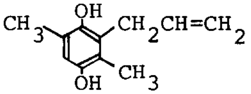
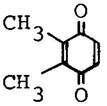
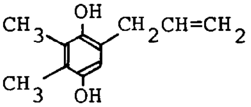
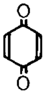
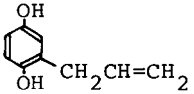
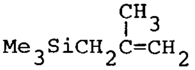
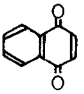
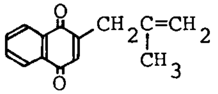
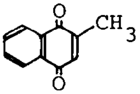
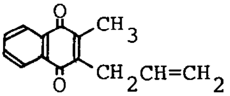
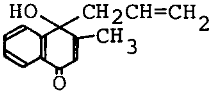
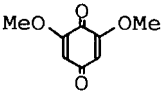
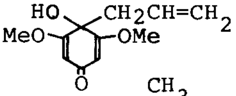
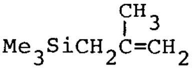
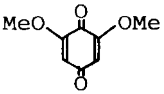
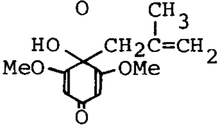
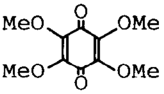
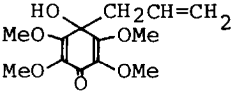
Table 1. Synthesis of allylhydroquinones and/or p-allylquinols from quinones and allylsilanes in the presence of titanium tetrachloride[a)]

Run	Allylsilanes	Quinones	Conditions (°C/min.)	Products	% Yield[b)]
1	$Me_3SiCH_2CH=CH_2$		0 / 45		55
2	 $Me_3SiCH_2C(CH_3)=CH_2$		-78 / 20	 c,d)	30
3	$Me_3SiCH_2CH=CH_2$		-78 / 10		47
4	$Me_3SiCH_2CH=CH_2$		-78 /120		58
5	$Me_3SiCH_2CH=CH_2$		-78 / 60		59
6	 $Me_3SiCH_2C(CH_3)=CH_2$		-78 /120	 c)	38
7	$Me_3SiCH_2CH=CH_2$		-45 / 15		7
					54
8	$Me_3SiCH_2CH=CH_2$		-78 / 30		81
9	 $Me_3SiCH_2C(CH_3)=CH_2$		-78 / 30		81
10	$Me_3SiCH_2CH=CH_2$		-78 / 20		91

a) Satisfactory spectral data and elemental analyses were obtained for all new compounds. b) Yields are based on purified products after isolation. c) Products after oxidation with iodine or ferric chloride. d) A mixture of geometric isomers(2,3-: 2,5-: 2,6- = 5: 32: 63).

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14) The present cases studied do not completely exclude the process via conjugate addition of the allylsilane to the quinone.[13)]
15) By the controlled experiment, it was found that the p-allylquinol, thus obtained, did not afford the allylnaphthoquinone under the reaction condition.
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