REDUCTIVE CLAISEN REARRANGEMENTS OF ANTHRAQUINONE ALLYL ETHERS Ian K. Boddy, Peter J. Boniface, Richard C. Cambie, Peter A. Craw, David S. Larsen, Hamish McDonald, Peter S. Rutledge, * and Paul D. Woodgate Department of Chemistry, University of Auckland, New Zealand

<u>Summary</u> Gentle heating of allyloxyanthraquinones with sodium dithionite in dimethylformamide — water effects a rapid and controlled rearrangement to give high yields of 2-allylanthraquinones.

Recently we reported^{1,2} on the Claisen rearrangements of the 1,4-bisallyloxyanthraquinones (1) and (2) as a possible method for introducing side chains in the 2- and 3-positions which would then be suitable for elaboration to the A-ring of an anthracyclinone. Although one of the allyl groups rearranged normally the second did so only sluggishly, thereby allowing other reactions to compete. In the case of anthraquinone (2) the problem was overcome by forming the anthrafuraquinone (3) from the product (8) of initial rearrangement, and then carrying out the second rearrangement.

We now report an alternative solution to the problem wherein the quinone carbonyls of the anthraquinone are reduced in situ to an anthrasemiquinone radical anion³ or dianion under conditions also suitable for Claisen rearrangement. Treatment of an allyloxy anthraquinone with sodium dithionite⁴ in dimethylformamide⁵ — water (1:1) with gentle heating effects a rapid and controlled rearrangement to the desired products in excellent yields (Table).

Table

Substrate ^a	Na ₂ S ₂ O ₄ (mol equiv.)	Time	Product b	Yield (%)
(10)	1.3	35 min	(13)	100
(11)	1.3	2 h	(14)	92
(12)	1.3	2 h	(15)	78
(3)	1.7	2 h	(6)	94
(4)	1.3	15 min	(5)	99
(2)	1.8	2.5 h	(8)	96

^a Reactions were carried out in DMF-H₂O (l:l). ^b All products were characterised by m.p., i.r., and ¹H n.m.r. spectral comparison with authentic samples or by combustion analysis. Treatment of the bisallyloxyanthraquinone (1) under the above conditions gave only a low (12%) yield of the 2,3-diallylanthraquinone (16) together with a number of other products, e.g. (9), whose yields depended on the time of the reaction. However, when the reaction was carried out with sodium dithionite (1.0 mol equiv.) in the presence of sodium hydroxide (4 mol equiv.) for 1 h the desired product (16) of double rearrangement was obtained in 72% yield. The ready formation of an anthrafuran was demonstrated when the reductive Claisen rearrangement was carried out on the chloroallyloxy compound (12) in the presence of sodium hydroxide. This afforded the compound (7) in 92% yield. In the case of the 1,4-bis(chloroallyl)ether (2) the products and yields depended on the conditions used. The highest yield (44%) of (17) was obtained when 1.5 mol equiv. of sodium dithionite was used with sodium hydroxide (5 mol equiv.) for 1 h.

References

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