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VINYL GROUP MIGRATION AND FORMATION OF SPIROCYCLOPROPANES ON TREATMENT OF 9-ETHYL VINYL ETHERS OF XANTHENE, THIOXANTHENE AND N-METHYL ACRIDAN WITH BASE

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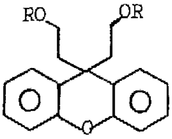
As a convenient source of the diol (1, R = H), xanthene was alkylated with 2-chloroethyl vinyl ether at room temperature with dimsyl sodium as base. Surprisingly, the major product was 9-(2-hydroxyethyl)-9'-vinyl xanthene (2); the expected di-vinyl ether (1, R = vinyl) accounted for 15% of the yield and a minor component was identified as xanthene 9-spirocyclopropane (3). At lower temperatures (0-5°C.), little rearrangement occurred and 1 (R = vinyl) was formed in high yield.



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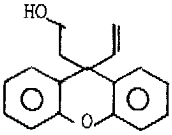

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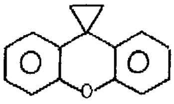

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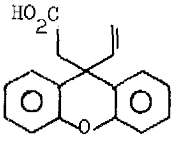

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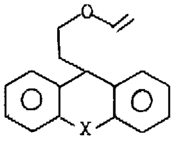
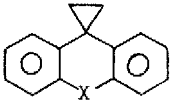
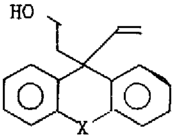
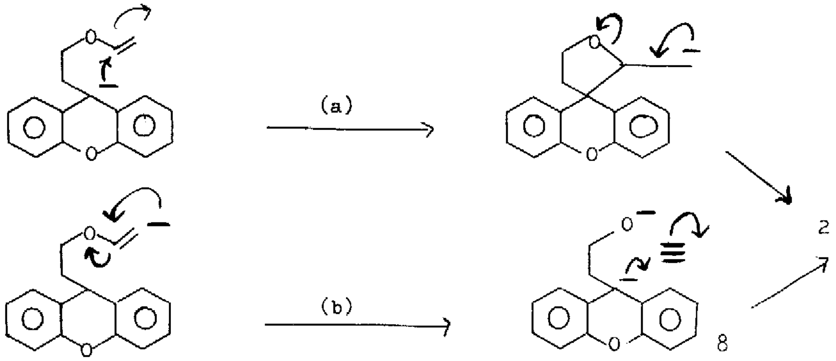
The structure (2), initially assigned on the basis of its p.m.r. spectrum, δ ($CDCl_3$) 2.2 (t, 3H, $-CH_2-$), 3.4 (t, 3H, $-CH_2-O-$), 5.1-6.4 (3H, vinyl group), 7-7.4 (8H, aromatic) was confirmed both by oxidative hydroboronation which gave the diol (1, R = H), m.p. 144-145°C; $^m/_e$ 270; δ ($CDCl_3$) 2.3 (t, 4H, two-CH_2-) 3.2 (t, 4H, two $-CH_2-O-$), 6.9-7.4 (8H, aromatic) identical to the acid hydrolysis product of the di-vinyl ether (1, R = vinyl) and, by oxidation to the acid (4), m.p. 134-135°C; $^m/_e$ 266; δ ($CDCl_3$) 3.0 (2H, $-CH_2-$), 5.0-6.4 (3H, vinyl group), 6.9-7.4 (8H, aromatic).

This type of vinyl shift appears to be novel although 1,2-vinyl migrations in Wittig rearrangements are well known[1]. The reaction provides a method of adding two functional carbon chains to certain reactive methylene groups, with possibilities for spiro-annelation operations. The sensitivity of the rearrangement to the nature of the anion is clearly shown by the behaviour of the monoalkylated compounds 5,6 and 7 under the reaction conditions (cf. Table).

	Yield, m.p. †	
		
5 X = O	30%, gum	70%, gum
6 X = S	70%, m.p. 119-120°C.	trace
7 X = NMe	60%, m.p. 105-106°C.	5%, m.p. 99-100°C.

The rearrangement may be rationalised as an addition-elimination mechanism (a) and has an intermolecular precedent[2] in the conversion of dihydropyran to non-4-en-1-ol with butyl lithium. An alternative fission-recombination interpretation (b) is unlikely since the di-anion (8), generated in an atmosphere of acetylene, failed to give 2.



† Satisfactory analytical and spectral data were obtained for all new compounds.

References

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2. F.L.M. Pattison and R.E.A. Dear, Can. J. Chem., 41, 2600, 1963.