Spirans. Part 10.[1] Acid-catalysed Rearrangement of Oxygen Heterocyclic Spirans.

By **Arthur W. S. Dick, Francis M. Dean,* David A. Matkin,** and **Malcolm L. Robinson,** The Robert Robinson Laboratories, The University of Liverpool, Liverpool L69 3BX

Hot trifluoroacetic acid isomerises the spiran (1) to the phenolic phenalene derivative (2), the structure of which is fully established. The isomerisation had previously been reported and a biradical intermediate suggested for it, but an ionic or an acid-catalysed [3,3] sigmatropic shift now offer better explanations.

Trifluoroacetic acid converts the spiran (10) into the dibenzoxanthylium cation (11a), a [3,3] sigmatropic shift now being prevented for steric reasons. The reactions probably involves heterocyclic ring opening to give a phenolic unsaturated ketone that cyclises to the cation in a conventional manner. This spiran is also sensitive to light which isomerises it to a phenolic oxepin derivative (14) that is readily oxidised by air to a quinone methide (15).

A similar xanthylium cation cannot be formed easily from the phenyl substituted spiran (18) because of the crowding caused by the substituent. A trace of the relatively unhindered cation (19) is formed, but the main reaction is diverted to a phenolic oxepin derivative (21) related to (14). It appears that a benzylic carbocation is formed and substitutes into the adjacent *peri*-position in the naphthalene ring.

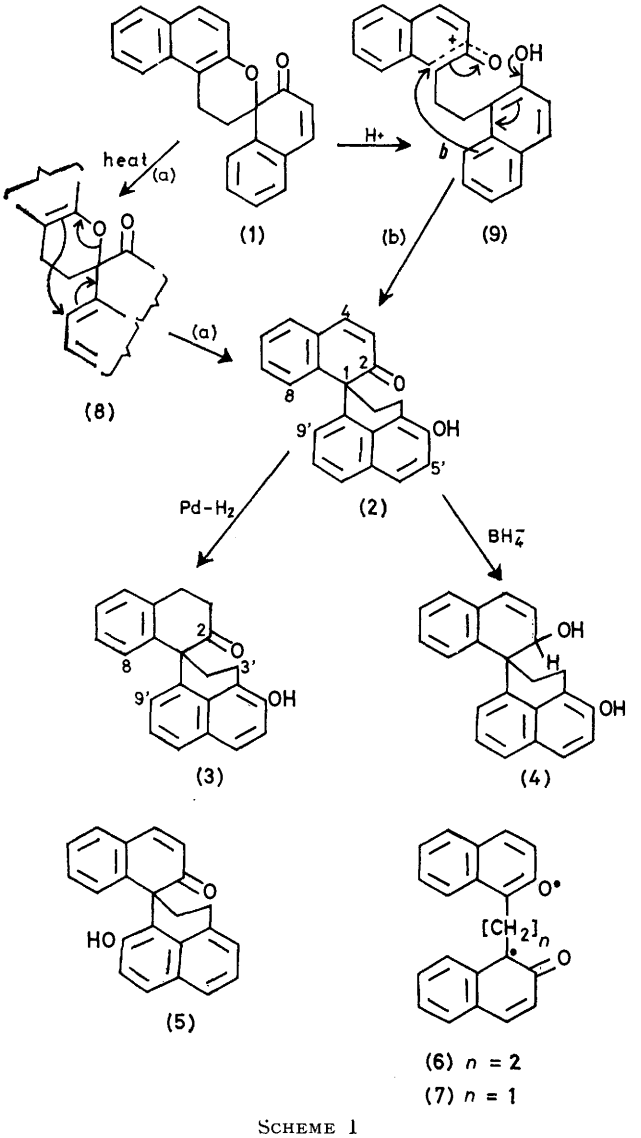
In order to establish the structure of the oxepin (21) a detailed analysis of the ^{1}H n.m.r. spectrum was undertaken and the hydroxy-group located by the local shifts generated in the methanesulphonate, a method preferable to dimethyl sulphoxide solvent shifts because of its much greater specificity.

FOLLOWING our own earlier work upon the acid-catalysed rearrangements of oxygen heterocyclic spirans [2,3] and the extensive work by Hey, Perkins, and their colleagues upon related nitrogen compounds [4] we have now studied the effect of hot trifluoroacetic acid upon three further spirans with a view to determining the steric effects of ring size and of bulky substitution upon the reaction.

Warm trifluoroacetic acid transformed the spiran (1) into the phenolic isomer (2) which gave an acetate. The i.r. spectrum indicated the conjugated carbonyl and hydroxy groups, and the n.m.r. spectrum (Table 1) indicated the presence of two linked methylene groups (one benzylic), a *cis*-vinylic grouping, and nine aromatic protons. Catalytic hydrogenation supplied the saturated ketone (3). In these compounds two aromatic protons consistently resonated at somewhat lower fields than the rest; these must be α-protons and it followed that two other α-positions must be occupied in a 2-naphthol nucleus. Borohydride reduction gave an alcohol shown by its n.m.r. spectrum (Table 1) to be the allylic alcohol (4) thus confirming the presence of the styryl ketone grouping in the original compound. Since these facts would fit structure (5) as well as structure (2) the latter was confirmed by a solvent shift method,[5] a change of solvent from deuteriochloroform to pyridine producing a down-

[1] Part IX, M. S. Chauhan, F. M. Dean, S. McDonald, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 359.
[2] D. J. Bennett, F. M. Dean, and A. W. Price, *J. Chem. Soc.* (*C*), 1970, 1557.
[3] M. S. Chauhan, F. M. Dean, K. B. Hindley, and M. L. Robinson, *Chem. Comm.*, 1971, 1141.
[4] D. H. Hey, *Quart. Rev.*, 1971, **26**, 483.
[5] R. A. W. Johnstone and C. C. Howard, *J.C.S. Perkin II*, 1974, 143; B. P. Hatton, C. C. Howard, and R. A. W. Johnstone, *Chem. Comm.*, 1973, 744; I. D. Entwistle, C. C. Howard, and R. A. W. Johnstone, *ibid.*, 1973, 464.

field shift (Δ τ 0.43) in the benzylic resonance only. Hence the phenolic hydroxy-group and the benzylic methylene group are adjacent. The same conclusion can be reached in another way. The spiran structure maintains the aromatic rings in perpendicular planes so that each has one proton projecting over the other (positions 8 and 9'). This explains why, throughout the

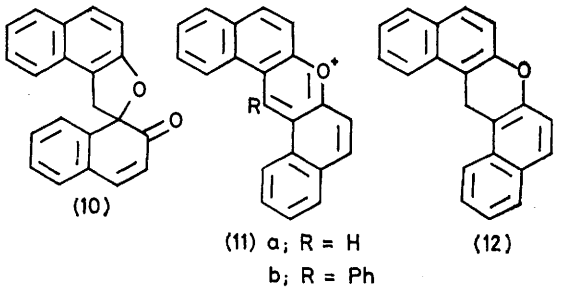


SCHEME 1

series (Table 1), two aromatic protons consistently resonate at fields greater than τ 3. In structure (5) only one aromatic proton could be shielded in this manner.

Compound (2) has already been reported briefly by Catterall [6] who obtained it by heating the spiran in hydrocarbon solvents at temperatures up to 190 °C or (slowly) in acetic acid under reflux and suggested that the biradical (6) might be the intermediate. We have failed to obtain more than traces of (2) from the resins formed in hydrocarbons; indeed we find that (2) itself resinifies under these conditions. But we have confirmed that a relatively smooth reaction occurs in acetic acid over long periods. We also find that dimethyl sulphoxide is a relatively good solvent for the isomerisation, and take these facts as evidence for some degree of ionic character and against purely radical intermediates for the reaction although the resins might be formed from these. Another reason against radical intermediates is suggested below. We would rather view the isomerisation as the sigmatropic shift indicated in (8) [Scheme 1; route (a)], with a proton shift to complete the transformation into (2). Related shifts are well known in allylic cyclohexadienones and are subject to marked acid catalysis; [7,8] acid would also catalyse the final proton transfer. Alternatively, we may be inducing the formation of a cation (9) followed by electrophilic substitution [Scheme 1, route (b)].

Accordingly, we next examined the spiran (10) the conformations of which are restricted by the single methylene link between the naphthalene residues, none being favourable for the formation of an analogue of (2) by either sigmatropic or cationic pathways. In agreement, this spiran was hardly affected by decalin at 190 °C. This fact also constitutes further evidence against the intervention by radical (6) mentioned above, for the similar radical (7) should have been formed and resulted in extensive decomposition by hydrogen abstraction and other reactions.



In hot trifluoroacetic acid the spiran (10) does not isomerise but yields the symmetrical xanthylium cation (11a) characterised by reduction to the xanthen derivative [9] (12). A 1,2-shift of (ether) oxygen could explain this result but is unlikely since in comparable cyclohexadienone derivatives alkyl groups migrate in preference to oxygen, [7,10,11] claims to the contrary being made only in cases where entirely different mechanisms are likely [3,12,13] or where the product may not have had the correct structure assigned to it. [14] Although

[6] G. Catterall, *Chem. Comm.*, 1974, 41.
[7] B. Miller, *Accounts Chem. Res.*, 1975, **8**, 245.
[8] B. Miller and M. R. Saidi, *Tetrahedron Letters*, 1975, 1365; 1972, 4391; J. Borgulya, R. Madeja, P. Fahrni, H.-J. Hansen, H. Schmid, and R. Barner, *Helv. Chim. Acta*, 1973, **56**, 14.
[9] M. Betti and C. M. Mundici, *Gazzetta*, 1905, **35**II, 37.
[10] V. P. Vitullo and E. A. Logue, *J. Org. Chem.*, 1973, **38**, 2265.
[11] R. S. Ward, *Chem. in Britain*, 1973, 444.
[12] A. M. Choudhury, *J.C.S. Perkin I*, 1974, 132.
[13] G. Brunow and M. Karhn, *J.C.S. Chem. Comm.*, 1976, 753.
[14] D. G. Hewitt, *J. Chem. Soc.* (C), 1971, 1750.

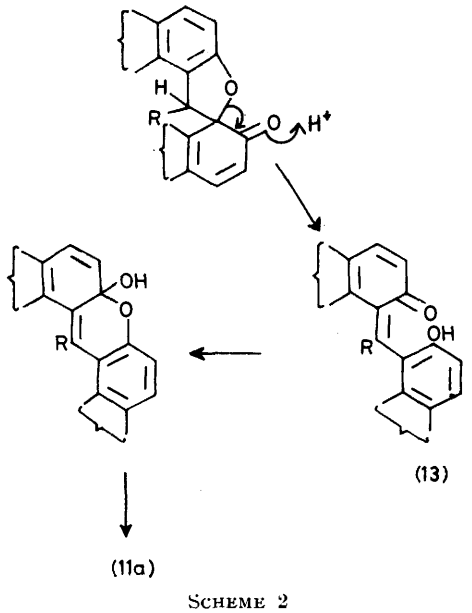
TABLE 1

^{1}H N.m.r. spectra [a] (τ scale) of compounds related to the the hydroxy-spiran (2)

Hydroxyspiran (2)			Acetate of (2)	Diol [b] (4)	Diacetate of (4)	Dihydrospiran (3)	Rel. Int.	Assignment
220 MHz $CDCl_3$	100 MHz DMSO	100 MHz Py	220 MHz $CDCl_3$	100 MHz $CDCl_3$	100 MHz $CDCl_3$	100 MHz $CDCl_3$		
					8.19		3	Alk·OCOCH$_3$
			7.63		7.68		3	Ar·OCOCH$_3$
7.74 (m)	7.89 (t, 6)	7.80 (m)	7.74 (m)	7.6 (m)	7.5 (m)	7.7 (m)	2	Ar·CH$_2$CH$_2$·Alk
7.01 (m)	7.10 (t, 6)	6.59 (t, 6)	7.04 (m)	7.0 (m)	7.1 (m)	*ca.* 7.1 (m)	2	Ar·CH$_2$·CH$_2$·Alk
						ca. 7.1 (m)	2	Ar·CH$_2$·CH$_2$·C:O
						6.78 (m)	2	Ar·CH$_2$·CH$_2$·C:O
				4.86 (dd; 3, 2)	3.69 (dd; 3, 2)		1	·CH:CH·CH·O
				4.06 (dd; 10, 3)	4.17 (dd; 10, 3)		1	·CH:CH·CH·O
3.76 (d, 10)	3.87 (d, 10)		3.76 (d, 10)				1	·CH:CH·C:O
2.44 (d, 10)	2.22 (d, 10)		2.44 (d, 10)				1	·CH:CH·C:O
3.13 (d, 8)	*ca.* 3.3 (m)		3.19 (d, 8)	3.4 (m)	3.42 (m)	3.32 (dd; 8,2)	2	ArH (shielded)
			3.06 (d, 8)			3.20 (dd; 8.2)		
2.34 (d, 9)	*ca.* 2.3 (m)		2.18 (dd; 8, 1)	*ca.* 2.4 (m)	*ca.* 2.2 (m)	2.40 (d, 8)	2	ArH[a]
2.27						2.32 (dd; 8, 1)		
5.1 [c]	0.3			4.0 [c] 7.9				OH

[a] Non-diagnostic aromatic resonances in the region 2—3 are not shown. Multiplicities and coupling constants (Hz) (in parentheses) are first order only. [b] Minor bands indicate the presence of an isomer. [c] Very broad bands removed by deuterium oxide.

alkyl shifts to carbonyl carbon are well documented for β-naphthalenones [7,15] they are excluded here because they would not give the correct product.



SCHEME 2

We conclude that the xanthylium salt (11a) is probably formed through an elimination giving (13), which could furnish the observed product by unexceptional means as shown in Scheme 2.

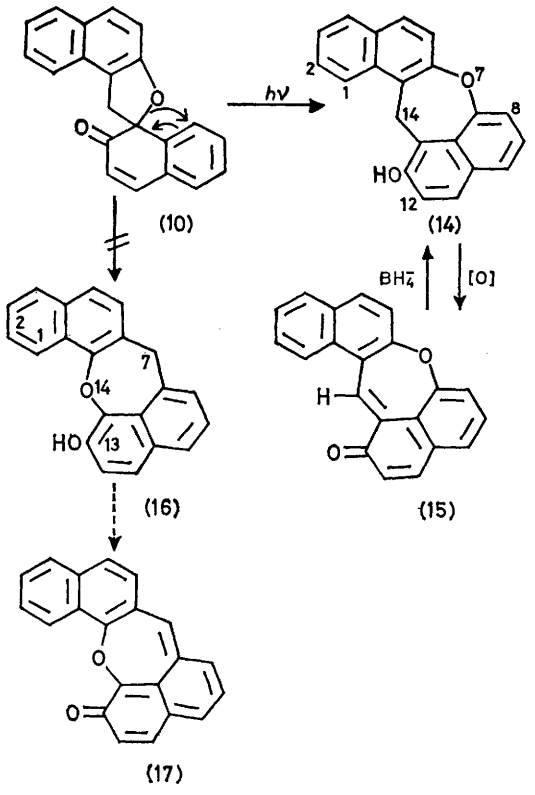
While working with the spiran (10) we noticed that it reddens when exposed to bright daylight and because the colour was reminiscent of that of the xanthylium salt we examined the reaction briefly. The reaction was slow and inefficient in daylight or artificial light and the primary product (apart from resin) was the phenol (14). The very ready oxidation by air gave the deeply orange-red quinone-methide (15), borohydride reduction regenerating the phenol (Scheme 3). The alternative formulation (16) is excluded because the n.m.r. spectrum (Table 2) does not permit structure (17), with so many vinylic protons, for the quinone methide. So great a loss of aromaticity would also be inconsistent with the ease of oxidation of the phenol. The exceptionally low field at which the 14-proton resonates in (15) (Table 2) was at first thought to indicate an aldehyde function but is entirely consistent with the combined deshielding effects of the naphthalene residue and the carbonyl group. The resonance near τ 1.6 allocated to the 1-proton in the phenol is discussed further in the sequel.

While this phenol might have been formed from the biradical intermediate (7) we prefer to regard the reaction as a 1,3-shift which is allowed photochemically (Scheme 3).

In order to avoid xanthylium salt formation we examined the spiran (18) of which both (racemic) geometrical isomers are available.[2,16] Models demonstrate that

[15] E. N. Marvell and J. L. Stevenson, *J. Amer. Chem. Soc.*, 1955, **77**, 5177.
[16] F. M. Dean and H. D. Locksley, *J. Chem. Soc.*, 1963, 393.

this spiran is most unlikely to furnish the symmetrical xanthylium salt (11b) when treated with acid. The



SCHEME 3

phenyl substituent would be very crowded; even when in a plane perpendicular to that of the rest of the molecule it is pinioned by the two naphthalene residues and there is an alternative route leading to structure (22). Structure (21) was confirmed by a detailed n.m.r. study with which the rest of this paper is concerned.

The new compound is a phenol not containing a carbonyl group. Its u.v. spectrum indicates the presence of only isolated aromatic chromophores. Its ^1H n.m.r. spectrum shows bands appropriate to one methine proton and sixteen aromatic protons, the analysis of which corresponds in the appropriate areas (protons assigned to rings A and B) to the analysis of the dibenzoxanthen derivative (23). The compound cannot itself be a dibenzoxanthen, although enough analogy exists [7,15] in β-naphthalenone chemistry for a rearrangement to structures such as (24), because its phenolic ring possesses no free *para*-position (does not respond to Gibbs' reagent) and there is no aromatic singlet in the n.m.r. spectrum.

The compound therefore contains a naphtho[1,8-*bc*]-oxepin nucleus on which the hydroxy-substituent has to be located. The molecule forms a shallow V and the phenyl substituent may be attached at position 14 so that it lies in the main plane or projects out of it. A position within the plane is most improbable because it is too congested and the system can be assumed to adopt the projecting phenyl conformation almost completely as in diagram (25). The protons at positions 2′ and 6′ must now patrol the shielding cones of the naphthalene rings and accordingly their resonances occur at the higher fields indicated in Table 3. Double-irradiation experiments disclosed a small interaction between these protons and the benzylic methine proton.

Table 3 sets out the n.m.r. assignments on the basis of structure (21), the position of the hydroxy-group being assumed for the moment and the protons designated by the numbers of the positions at which they are attached. The simplest spin systems are those in rings B and C, each

TABLE 2

^1H N.m.r. data [a] (τ scale) for oxepin (14) and its relatives.

	Field (MHz)	Solvent	Me	C(14)H	C(1)H	CH:CH·C:O	CH:CH·C:O
Oxepin [b] (14)	100	[$^2H_6$]Acetone		4.98 (2 H)	1.60 (d; 9)		
Acetate of (14)	60	$CDCl_3$	7.43	5.18 (2 H)	1.78 (dd; 8, 2)		
Oxepinone (15)	60	F_3CCO_2H		−0.8 (1 H)	1.96 (d; 8)	2.11 (d; 10)	3.04 (d; 10)

[a] Aromatic resonances are not shown. Multiplicities and coupling constants (m; Hz) are first order only. [b] Hydroxylic resonance appeared at 1.22 (1 H) as a fairly sharp singlet removed by addition of D_2O.

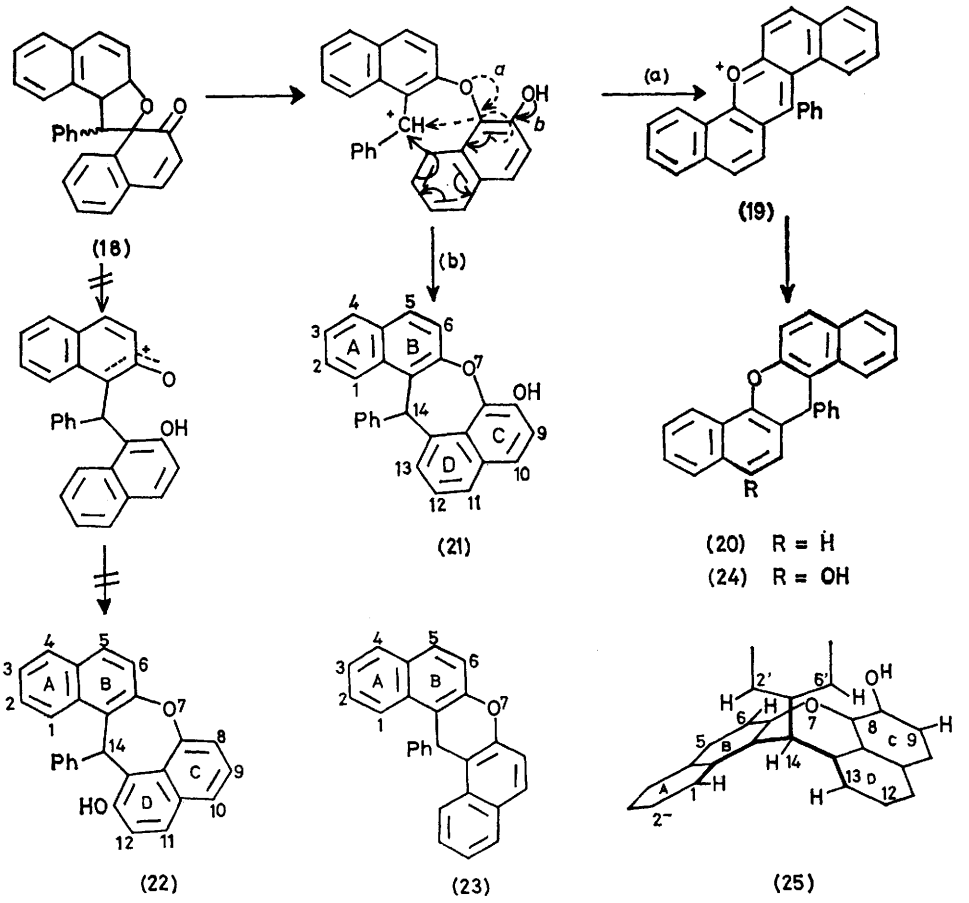
the same situation holds for the hypothetical intermediates in Scheme 2 (R = Ph). A xanthylium salt is indeed formed in traces by acid treatment, but it is the less hindered, unsymmetrical isomer (19) resulting from a benzylic 1,2-shift to carbonyl carbon (Route *a*, Scheme 4). It was characterised by reduction to the dibenzoxanthen (20).

The main effect of acid upon the spiran (18) (either isomer) is to isomerise it to an oxepin derivative (21) similar to (14). As shown in Scheme 4, route (b), the process is readily understood as formation of a benzylic carbocation ion and substitution into the adjacent *peri*-position in the naphthalene ring. Since phenoxylium ions are now also an established species,[17] however, consisting of pairs of doublets because of *ortho* (αβ) coupling. Protons 6 and 9 should give signals at relatively high fields because they are β-protons and because they are attached to rings bearing oxygen (hydroxy or ether) groupings. The ether may have less influence than the hydroxy oxygen because the V shape of the molecule prevents a full contribution from $p\,\pi$ overlap, and proton 6 should also be subject to some deshielding

[17] R. A. Abramovitch, M. Inbasekaran, and S. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 5428; R. A. Abramovitch, G. Alverne, and M. N. Inbasekaran, *Tetrahedron Letters*, 1977, 1113; U. Palmquist, A. Nilsson, V. D. Parker, and A. Ronlán, *J. Amer. Chem. Soc.*, 1976, **98**, 2571; W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 2026, A. B. Suttie, *Tetrahedron Letters*, 1969, 3727; J. W. A. Findlay, P. Gupta, and J. R. Lewis, *Chem. Comm.*, 1969, 206.

by ring C, so it is reasonable to associate proton 9 with the doublet at highest field (τ 2.75), and proton 6 with that at the next highest field (2.66). Suitable partner ambiguity about which lines were to be associated (Table 4). Thus protons 5,6,9, and 10 have been identified.

One signal stands out from the others at a much lower



SCHEME 4

TABLE 3

^{1}H N.m.r. spectral data (220 Hz) for the oxepin derivative (21) and xanthen derivative (23)

	A Oxepin (21) in $CDCl_3$		B Oxepin (21) in $(CD_3)_2SO$	B − A	C Xanthen (23) in $CDCl_3$	C − A
Proton	τ	*J*	τ	p.p.m.	τ	p.p.m.
1	1.56	8, *m* [a]	1.24	−0.32	1.66	+0.10
2	2.36	8, 6.5, *m*	2.30	−0.06	2.47	+0.11
3	2.51	8, 7, *m*	2.45	−0.06	2.64	+0.13
4	2.13	8.0, *m*	1.99	−0.14	2.23	+0.10
5	2.23	8.5	2.06	−0.17	2.24	−0.01
6	2.66	8.5	2.79	+0.13	2.55	−0.11
9	2.75	8.5	2.39	−0.36		
10	2.46	8.5	2.39	−0.07		
11	2.29	8.0, *m*	2.19	−0.10		
12	2.72	6.5, 8.0	2.68	−0.04		
13	2.43	6.5, *m*	2.21	−0.22		
14	3.67		3.47	−0.20	3.55	−0.12
2′, 6′	3.07	complex	3.18	+0.11	3.05	−0.02
3′, 4′, 5′	2.85	complex	*ca.* 2.8	±0	2.89	+0.04

[a] Further splitting generally not well resolved, is thought to be essentially *meta*-splitting and is designated by *m*.

doublets for these occur at 2.46 and 2.23, and all show the same splitting (8.5 Hz) appropriate to αβ-coupling. Doubling-resonance experiments were not easily carried out because some of the lines are close, but there was no field (1.56); it takes the form of a doublet with a splitting (8 Hz) indicative of αβ-coupling, but it also shows broadening indicative of *meta* and/or other long-range coupling. Proton 1 seems to be the only one that could

generate such a signal; not only is it an α-proton, it is also the only one that would be subject to further deshielding by an adjacent *peri*-substituent. Ring D should contribute a deshielding effect, about 0.2 p.p.m. according to the Johnson–Bovey plot [18] for benzene. Proton 1 also lies within the deshielding cone of the phenyl substituent which must, therefore, make yet another contribution. In the similar oxepin (16) there is no phenyl substituent but there is now a hydroxy-group at position 13 that approaches proton 1 close enough (*ca.* 3 Å) to exert other types of deshielding influence.[19]

Irradiation of proton 1 affects only a complex multiplet centred at 2.36 which is, therefore, assigned to proton 2 (Table 4). The multiplet collapses to a doublet with a splitting (6.5 Hz) due to ββ-coupling with proton 3 and a minor splitting expected from the *meta*-proton at position 4. There are two more such multiplets in the spectrum, one to be assigned to proton 3 and the other to proton 12. Of these protons it is the latter that can be identified easily because of its relation to the hydroxy-group, changes at this producing marked effects upon its chemical shift. From an electronic point of view, position 12 in a 2-naphthol nucleus is comparable with the *para*-position in simple phenols for which such shifts are well documented.[20] Thus acetylation produces a downfield shift of 0.14 p.p.m. in the multiplet at 2.72 while not affecting the two other multiplets (Table 5). The complex multiplet at 2.51 therefore originates from proton 3, and protons 2,3, and 12 have now been identified.

Protons 4, 11, and 13 remain, and the spectrum contains three appropriate doublets. Those at 2.29 and 2.48 are strongly affected by irradiation of proton 12, whereas the third, at 2.13 is not and must represent proton 4, the splitting (8 Hz) corresponding correctly to αβ-coupling (Tables 3 and 4). Protons 11 and 13 can be distinguished clearly since the doublet at 2.29 shows a splitting (8 Hz) appropriate to αβ-coupling while the other doublet (6.5 Hz) is subject to ββ-coupling.

The n.m.r. spectrum of the symmetrical dibenzoxanthen derivative [21] (23) affords a general confirmation of the assignments to the regions around rings A and B. An exact parallel in chemical shifts cannot be expected because the V shape of the xanthen is much flatter than that of the oxepin, the phenyl substituent projects at a different angle over the main plane and is more free to rotate, and the naphthalene residues are not similarly aligned. Nevertheless, the bands assigned to protons 1—6 fall in the same order (Table 3) and the splittings are very similar in the two series. Generally, bands

TABLE 4

Double irradiation of oxepin derivative (21), at 220 MHz, in $CDCl_3$

Line (τ) irradiated	Proton saturated [a]	Protons affected: strongly	Protons affected: weakly	Protons not affected	Protons not observable [b]
3.66	14		2′, 6′	1—6, 9—14, 3′—5′	
2.79 [c]	9, (12)		10, 13	1—6, 11? 14, 2′—6′	
2.75	9, 12	10, 13	11	1—5, 14, 2′—6′	6
2.69	(6), (9), 12	11, 13	5, 10	1—4, 14, 2′—6′	
2.67	6, (9), 12	5, 11	10, 13	1, 2, 4, 14, 2′—6′	3
2.37	2, (11)	1	5, 6, 12	3, 4, 9, 2′—6′	10, 13
1.56	1	2		3—6, 9—14, 2′—6′	

[a] Where lines are close, a parenthesis indicates that a line adjacent to the irradiation must be affected to some extent short of saturation. [b] Because the irradiation energy obscured them, or because they could not be certainly recognised in the modified spectrum. [c] At a relatively low energy so as to preserve the maximum information in the rest of the spectrum.

TABLE 5

^1H N.m.r. spectra of the acetate of the oxepin (21), at 220 MHz (τ scale)

Proton	A Oxepin (21) ($CDCl_3$)	B Acetate ($CDCl_3$)	B − A (p.p.m.)	C Acetate [$(CD_3)_2SO$]	C − B (p.p.m.)
1	1.56	1.58	+0.02	1.23	−0.35
2	2.36	2.38	+0.02	2.29	−0.09
3	2.51	2.52	+0.01	2.43	−0.09
4	2.13	2.14	+0.01	1.98	−0.16
5	2.23	2.23	±0	2.03	−0.20
6	2.66	2.71	+0.05	2.62	−0.09
9	2.75	2.76	+0.01	2.70	-0.06
10	2.46	2.40	−0.06	2.03	−0.37
11	2.29	2.24	−0.05	2.22	−0.02
12	2.72	2.58	−0.14	2.46	−0.12
13	2.43	2.40	−0.03	2.06	−0.34
14	3.67	3.68	+0.01	3.38	−0.30
2′, 6′	3.07	3.10	+0.03	3.26	+0.16
3′, 4′, 5′	2.85	2.89	+0.04	2.87	−0.02
CH_3		7.58		7.56	−0.02

[18] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[19] J. B. Carr and A. C. Huitric, *J. Org. Chem.*, 1964, **29**, 2506; R. V. Lemieux and J. D. Stevens, *Canad. J. Chem.*, 1966, **44**, 249.

[20] (*a*) R. G. Cooke and I. D. Rae, *Austral. J. Chem.*, 1964, **17**, 379; (*b*) E. Ritchie, W. C. Taylor, and S. T. K. Vautin, *ibid.*, 1965, **18**, 2021.

[21] J. T. Hewitt and A. J. Turner, *Ber.*, 1901, **34**, 202.

appear at higher fields in the xanthen than in the oxepin, so that the reverse shift in proton 6 is significant. Models show that in the oxepin the phenyl substituent leans over the main plane towards proton 6, which therefore finds itself almost over the plane of the benzene ring and at a distance of *ca.* 4 Å from it. In this arrangement a shielding of up to 0.2 p.p.m. can be expected.

It is obvious that structure (22) has not been excluded as it must yield a very similar spectrum. To emphasize this point, structure (22) is not numbered systematically but in accordance with the n.m.r. analysis. In order to locate the hydroxy-group securely it seemed best to relate this not with its own naphthalene moiety but with the opposite one, rings A and B being the same and identifiable in both isomers, and in particular with protons 1, 6, 13, and 14. An attempt was made to apply the solvent-shift technique [5] since hydrogen-bonded dimethyl sulphoxide would be expected to induce local shifts depending in magnitude and sign upon distance and orientation factors. This solvent did strongly influence protons 1, 6, 13, and 14 as well as 9, the proton *ortho* to the hydroxy-group (Table 3), a result that appeared to favour structure (22) rather than (21). A referee pointed out that some of these effects could be due to association of the solvent with the phenol in ways additional to hydrogen bonding, and that this is the case was first indicated by the solvent shifts induced in the acetate (Table 5). Although hydrogen bonding is now excluded, marked shifts appear in several resonances including those of protons 1, 13, and 14. We next examined the effect of mixtures of trichloromethane and dimethyl sulphoxide instead of neat sulphoxide on the assumption that other modes of association would be less energetically favourable than hydrogen bonding and would be diminished selectively. Table 6 shows that shifts for protons 6 and 9 remain large when others have greatly diminished, and structure (21) is favoured thereby. Presumably in neat sulphoxide there will usually be a solvent molecule more or less settled within the cleft of the V shaped system and capable of affecting protons in its vicinity. The sulphoxide shifts seen in the spectrum of the acetate (Table 5) must originate in this manner, hydrogen bonding now being impossible and protons 6 and 9 not much affected.

In order to obtain more definitive evidence we sought to associate the hydroxy-group with anisotropic shielding effects in a more specific fashion, and therefore examined the methanesulphonate in trichloromethane. As shown by Table 6, the shifts are now much more limited; importantly, protons 1 and 14 are hardly affected whereas proton 6 is strongly modified. Again because of the V shape of the molecule, the rather long sulphur–oxygen bond allows the sulphur atom to approach proton 6 as closely as proton 9 though not at a similar angle. Proton 12 is again affected, but only in the way alluded to in discussing the results of acetylation. Hence the hydroxy-group is close to proton 6 but not to protons 1 or 14, and structure (21) is established.

TABLE 6

Variations in the ^1H n.m.r. spectrum of oxepin (21) induced by partial solvation [a] with dimethyl sulphoxide and by methanesulphonate formation (τ scale).

Proton	A Oxepin (21) ($CDCl_3$)	B Oxepin (21) (mixture)	B — A (p.p.m.)	C Methane-sulphonate	C — A (p.p.m.)
1	1.56	1.46	−0.10	1.57	+0.01
2	2.36	*b*		2.34	−0.02
3	2.51	2.48	−0.03	2.43	−0.08
4	2.13	2.10	−0.03	2.09	−0.04
5	2.23	2.19	−0.04	2.19	−0.04
6	2.66	2.82	+0.16	2.50	−0.16
9	2.75	2.37	−0.38	2.50	−0.25
10	2.46	2.48	−0.02	2.38	−0.08
11	2.29	2.37	+0.08	2.20	−0.09
12	2.72	2.74	+0.02	2.52	−0.20
13	2.43	2.30	−0.10	2.35	−0.08
14	3.67	3.56	−0.09	3.69	+0.02
2′, 6′	3.07	3.13	−0.06	3.17	+0.10
3′, 4′, 5′	2.85	2.92	−0.07	2.90	+0.05
CH_3				7.26	

[a] Obtained by examining the compound in a mixture of deuteriotrichloromethane and dimethyl sulphoxide (1 : 1; v/v). [b] The appropriate bond could not be securely identified.

The methanesulphonate group may prove to be a suitable probe of the environment of hydroxy-groups in other complex molecules, a point that we hope to pursue. At present we are aware only of reports [20b] that arylsulphonate groups are not useful in this respect, which is not surprising since ambiguity must arise from the presence of two anisotropic groups that may act in opposition.

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 60—80 °C. U.v. spectra were determined on solutions in ethanol. I.r. spectra were determined on mulls in paraffin if no other medium is stated, and only diagnostic bands are reported.

2′,3′,-Dihydro-4′-hydroxyspiro[naphthalene-1(2 H),1′-phenalen]-2-one (2).—(i) The spiran [22] (1) (0.2 g) isomerised in dimethyl sulphoxide (20 ml) held at 160 °C for 5 h and the product was isolated by dilution with water and extraction

[22] M. S. Chauhan, F. M. Dean, D. Matkin, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 120.

into ether. The extract was concentrated and light petroleum added to precipitate the product which, repeatedly recrystallised from acetone–light petroleum (best) or benzene, gave the hydroxy-spiran as tiny yellow prisms (0.08 g), m.p. *ca.* 242 °C, $\nu_{max.}$ (KBr) 3 200 (OH), 1 633 (C : O) (both hydrogen-bonded), $\nu_{max.}$ ($CHCl_3$) 3 400 (OH), 1 660 cm^{-1} (C : O) (Found: C, 84.3; H, 5.1%; *M*, 312. Calc. for $C_{22}H_{15}O_2$: C, 84.6; H, 5.2%; *M*, 312). The *acetate* crystallised from light petroleum as prisms, m.p. 154—156 °C, $\nu_{max.}$ 1 750 (OAc), 1 645 cm^{-1} (conj. C : O) (Found: C, 81.1; H, 5.3%; *M*, 354. $C_{24}H_{18}O_3$ requires C, 81.3; H, 5.1%; *M* 354).

(ii) The spiran (1) (0.2 g) was kept in trifluoroacetic acid (20 ml) at 75 °C for 20 min. The solution was diluted with much water and extracted repeatedly with ether; the extract was washed with aqueous sodium hydrogen carbonate and then dried and treated as in (i). Alternatively, the acid was removed from the reaction mixture under reduced pressure and the residue was chromatographed on silica from chloroform and benzene–diethyl ether before crystallisation. In either case the product supplied the hydroxy-spiran as prisms (0.09 g), m.p. *ca.* 242 °C, identical with the compound from (i).

(iii) The spiran (1) was heated in dodecane or tetralin at the b.p. under nitrogen until t.l.c. showed that none was left.[6] Concentration of the solution under reduced pressure then gave an extremely resinous product from which repeated chromatography on silica from chloroform or from benzene–diethyl ether separated a small fraction that appeared from t.l.c. and spectral characteristics to consist mainly of the hydroxy-spiran (2) but which failed to crystallise and resisted further purification. Similarly heated in tetralin, the hydroxy-spiran (2) itself gave a resinous product with these features.

2′,3′-Dihydrospiro[naphthalene-1(2H)-1′-phenalene]-2,4′-diol (4).—Sodium borohydride (10 mg) in water (0.5 ml) was added to the hydroxy-spiran (14) (100 mg) in warm ethanol (5 ml). After 1.5 h, addition of water precipitated a solid (110 mg) which appeared from spectral analysis to consist of a mixture of stereoisomers corresponding to the diol (4) but which could not be satisfactorily resolved by chromatography on silica or crystallisation; the best product consisted of prisms (30 mg), m.p. 105—110 °C. With acetic anhydride and pyridine, however, this material furnished the related *diacetate*, m.p. 178—179 °C, $\nu_{max.}$ 1 735 (OAc) and 1 600 cm^{-1} (aromatic) (Found: C, 78.4; H, 5.6%; *M*, 398. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.6%; *M*, 398)

2′,3,3′,4-Tetrahydro-4′-hydroxyspiro[naphthalene-1(2 H),-1′-phenalen]-2-one (3).—The hydroxy-spiran (2) (0.2 g) in ethyl acetate (20 ml) was shaken under hydrogen with palladinized charcoal (10%; 50 mg) until uptake of gas had ceased. The brownish gum left after evaporation of the filtrate crystallized from methanol giving the *dihydrospiran* as a crystalline powder (67 mg), m.p. 199—200 °C, $\nu_{max.}$ 3 290 (OH), 1 685 (C : O) (both hydrogen bonded), 1 630, 1 600, 1 585, 1 520, and 1 500 cm^{-1} (aromatic) (Found: C, 83.5; H, 5.7%; *M*, 314. $C_{22}H_{18}O_2$ requires C, 84.0; H, 5.8%; *M*, 314).

Reactions of the Spiran (10).—(i) *With acid.* The spiran (0.2 g) in refluxing trifluoroacetic acid gradually gave a dark solution and when t.l.c. showed that none remained (*ca.* 15 h) the solution was concentrated under reduced pressure to remove nearly all the acid. The residue was dissolved in acetic acid and perchloric acid was added until precipitation was complete. The intensely red crystalline solid (70 mg), m.p. 326 °C (decomp.), so obtained was spectroscopically identical with authentic dibenzo[*a*,*j*]xanthylium perchlorate. In a second experiment the residue was dissolved in methanol and treated with an excess of methanolic sodium borohydride for 2 min. Removal of the solvent left a solid which, after purification on silica from light petroleum, crystallized from acetone giving dibenzo[*a*,*j*]xanthen (12) (62 mg), m.p. 203—205 °C, indistinguishable from an authentic specimen.

(ii) *Photochemical isomerisation.* Several experiments in which the spiran was irradiated in various ways all gave complex results. In a typical example, the spiran (0.5 g) in benzene or methanol (150 ml) was either left in bright daylight or diffuse sunlight for several days or placed in a Pyrex tube (length, 30 cm; internal diameter, 8 cm) cooled by water at 24 °C and de-aerated by a stream of nitrogen for 30 min. and then irradiated by a Phillips ' Ultraphil ' (MLU 300 W) u.v. lamp for 8 h. Evaporation of the solution gave a dark red residue which was chromatographed on silica from benzene–dichloromethane to give in the first eluates the starting spiran (10) (0.23 g) along with the *o*-quinone methide (15), *13H-dinaphtho[1,8-bc:1,2-f]oxepin-13-one*, which crystallised from butan-2-one as orange needles (14 mg), m.p. 121—122 °C (decomp.), $\lambda_{max.}$ 270, 338, and 440 nm (log ε 3.97, 3.70, and 3,31), $\nu_{max.}$ 1 645 (conj. C : O), 1 590, 1 560, and 1 515 cm^{-1} (ethylenic and aromatic) (Found: C, 85.1; H, 4.2%; *M*, 296. $C_{21}H_{12}O_2$ requires C, 85.1; H, 4.1%; *M*, 296). Later eluates supplied the corresponding phenol, *14H-dinaphtho[1,8-bc:1,2-f]oxepin-13-ol* (14), which formed needles (from benzene) (49 mg), m.p. 182—185 °C (decomp.), $\lambda_{max.}$ 286, 325, and 345 nm (log ε 3.93, 3.58, and 3.57), $\nu_{max.}$ 3 300 (OH), 1 630w, 1 600, 1 585, and 1 515 cm^{-1} (aromatic) (Found: C, 84.4; H, 5.0%; *M*, 298. $C_{21}H_{14}O_2$ requires C, 86.6; H, 4.7%; *M*, 298). This compound is believed to be without colour when pure but is so easily attacked by air that even the dry solid becomes coated with red and the alkaline solution precipitates the orange quinone methide almost immediately and quantitatively. Conversely, the orange quinone methide (15) (30 mg) in methanol (2 ml) is at once bleached by the addition of sodium borohydride (10 mg) in water (1 ml) and the phenol (14) is obtained upon acidification by chilled hydrochloric acid if air is excluded. With acetic anhydride and pyridine under nitrogen, the phenol gave the *acetate* which separated from methanol as colourless needles, m.p. 130—132 °C, $\lambda_{max.}$ 292 and 324 nm (log ε 4.0 and 3.5), $\nu_{max.}$ 1 745 (OAc) 1 625w, 1 600, 1 580, and 1 515 cm^{-1} (aromatic) (Found: C, 81.3; H, 4.7%; *M*, 340. $C_{12}H_{16}O_3$ requires C, 81.3; H, 4.7%; *M*, 340).

14-Phenyl-14H-dinaphtho[1,8-bc:1,2-f]oxepin-8-ol (21).—The spiran (18) (either stereoisomer A or B[2]) (0.20 g) was kept in refluxing trifluoroacetic acid (15 ml) for 8 h. When cooled the solution furnished a pink, granular solid (0.16 g) which, after purification from acetone, supplied the *phenyloxepinol* as prisms, m.p. 263—265 °C (decomp.), $\lambda_{max.}$ 288, 297sh, 328, 335, and 344 nm (log ε 2.98, 3.87, 3.56, 3.58, and 3.61), $\nu_{max.}$ 3 500 (OH), 1 630 and 1 605 (aromatic) (Found: C, 86.4; H, 4.8%; *M*, 374. $C_{27}H_{18}O_2$ requires C, 86.6; H, 4.9%; *M*, 374). The *acetate* separated from methanol as prisms, m.p. 209—212 °C, $\nu_{max.}$ 1 745 (OAc), 1 625, 1 600, and 1 585 cm^{-1} (aromatic) (Found: C, 83.3; H, 4.8%; *M*, 416. $C_{29}H_{20}O_3$ requires C, 83.6; H, 4.8%; *M*, 416). Obtained by the use of methyl sulphate and potassium carbonate in refluxing acetone, the *methyl ether* crystallised from tetrachloromethane as prisms, m.p. 227—229 °C, $\nu_{max.}$ 1 625, 1 600, and 1 575 cm^{-1} (aromatic) (Found: *M*, 388.146 35. $C_{28}H_{20}O_2$ requires *M*, 388.146 32). The *methanesulphonate*

(from methanesulphonyl chloride and pyridine at 0 °C for 12 h) crystallised from ethyl acetate or acetone as prisms, m.p. 155—157 °C (Found: C, 73.9; H, 4.4%; *M*, 452.1118. $C_{28}H_{20}O_4S$ requires C, 74.3; H, 44%; *M*, 452.1082).

The dark acid solution left after removal of the phenyloxepinol was concentrated to remove most of the acid and residue ground with methanol. A small amount of residual phenyloxepinol did not dissolve and was removed. The solution was treated with an excess of methanolic sodium borohydride and the precipitate rejected. The solution was concentrated *in vacuo* and the gum left was purified by chromatography on silica from ether–light petroleum (1 : 99) which furnished eluates containing 14-phenyl-14*H*-dibenzo-[*a*,*h*]xanthen (20) which separated from ethyl acetate as needles (18 mg), m.p. 217 °C (decomp.) identical with an authentic specimen and having $\nu_{max.}$ 1 620, 1 595, 1 515, 1 495, 1 435, 1 405, 1 285, 1 260, 1 245, 1 190w, 1 145w, 1 085, 1 090, 1 035w, 1 015, 960w, 955w, 930w, 925w, 890w, 880w, 830, 820, 805, 780, 755, 735, and 720. The isomeric 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthen has $\nu_{max.}$ 1 630sh, 1 625, 1 595, 1 520, 1 495w, 1 435, 1 410, 1 255, 1 240, 1 210w, 1 155w, 1 095, 1 040w, 975, 870w, 840, 820, 755, 760, 730, 710cm^{-1}.

[7/155 *Received*, 31*st January*, 1977]