191. Halogenation of Xanthenyl and Thioxanthenylallenes

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Summary

Reactions of acids with vinylidenexanthenes (or thioxanthenes) **1** and 9-methoxy-9-vinylxanthenes (or thioxanthenes) **8** give xanthene- (or thioxanthene-) 9-spiro-1′-indenes **7**. With bromine or sulfuryl chloride they give the corresponding 2′-halogenoxanthene- (or thioxanthene-)9-spiro-1′-indenes **5**. Formation of such derivatives depends on preferential attack of the reagents on allenes **1** to give initially xanthylium (or thioxanthylium) ions **3** which cyclize. One π bond of the allenes **1** can be selectively reduced in acid media. Chemical and spectral evidence for these routes are presented.

Recently we reported on the cyclization of vinylidenexanthenes (**1**, Y=O, R=alkoxy) in acid media which give xanthene-9-spiro-1′-indenes (**7**, Y=O) [1]. This cyclization revealed the preferential reactivity of the π bond of the involved xanthene residue. We have subsequently investigated reactions of equimolecular quantities of either bromine or sulfuryl chloride with vinylidenexanthenes and thioxanthenes (**1**, Y=O or S, R=alkoxy) in order to have further insight on the behaviour and reactivity of such polyarylallenes towards halogenation.

Addition of bromine took place readily with instantaneous development of very deep blue-violet colour instead of the normal discharge of bromine colour. The same colour developed on addition of sulfuryl chloride to **1** (Y=O or S) in carbon tetrachloride solution. This suggested that heteroatom in this type of compound would be responsible for development of such colour [1] as it may encourage migration of one halogen atom due to concerted electron-shift in **2** with formation of the coloured oxonium derivative **3**. On the other hand, addition may take place through an initial cation attack on the activated central carbon atom of **1**, rather than free radical addition to give **3** (Y=O or S). On heating solutions of **3** (Y=O or S, R=alkoxy) ready evolution of hydrogen halide occurred, affording mainly the corresponding 2′-bromo-6′-alkoxy-3′-aryl-xanthene- (or thioxanthene-)9-spiro-1′-indenes **5** (Y=O or S, X=Br, R=alkoxy). When bromine was added to **1** (Y=O, R=OMe) and the reaction mixture was left 2 h at RT., the deep blue-violet crystals isolated were identified as the tribromide **4** (Y=O, X=Br, R=OMe), in addition to the corresponding bromoindene **5**. Compound **4** could be formed by addition of some liberated hydrogen bromide to **3**. Formation of bro-

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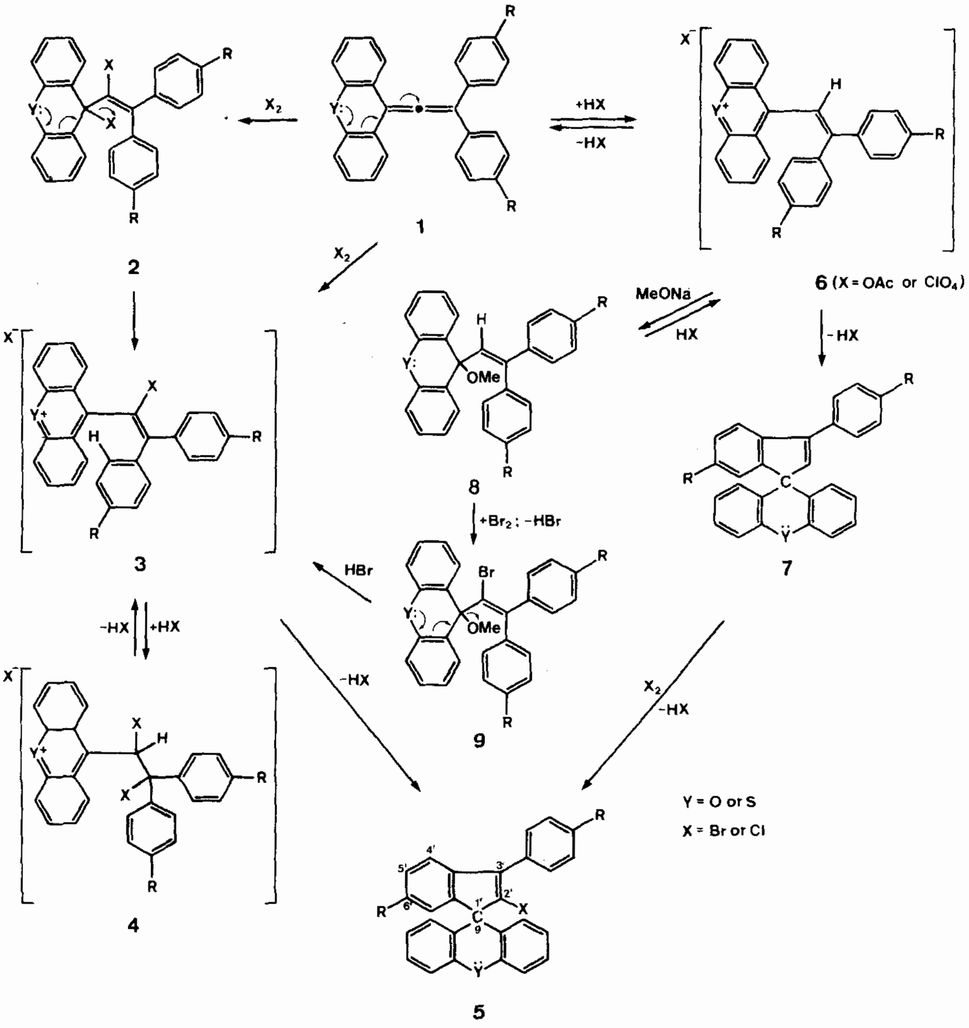
moindenes **5** provides good evidence for the site of preferential attack of halogen on **1**. The existence of an allylic carbonium ion [2] in such a system is not favoured owing to delocalization of positive charge over the central ring of the xanthenyl (or thioxanthenyl) moiety. Bromoindenes **5** are presumably formed *via* electrophilic attack of the 9-xanthylium (or 9-thioxanthylium) cation on one of the aryl groups [3] which was brought into the same plane through 90° rotation after initial attack. The ready elimination of hydrogen halide suggested that this cyclization proceeds with a relatively faster rate when compared with typical examples of xanthylium acetates or perchlorates **6** (Y = O, X = OAc or ClO_4) [1]. This could be attributed to the good leaving character of halogen in addition to steric interactions of attached halogen on the central carbon atom of **3** (Y = O or S, X = Br or Cl). On the other hand, thioxanthylium derivatives **3** (Y = S, X = Br or Cl) or **6** (Y = S,



X=OAc or ClO_4) need a relatively longer time to accomplish such rearrangements when compared with oxygen analogues.

The structure of 2′-bromo (or chloro) indenes **5** (Y=O or S, X=Br or Cl) had been confirmed by their preparation by either bromination or chlorination of the corresponding spiro-indenes **7** (Y=O or S), this reaction not being accompanied by colour development. Structure **5** was also supported by elemental analysis and ^{1}H-NMR. spectrum (with R=OMe) which clearly showed the non equivalency of the *p*-OMe groups (2 *s*, each 3 H, *J* = 12 Hz).

Thioxanthene-spiro-indenes **7**, like their oxygen analogues [1], were obtained by heating the corresponding allene **1** (Y=S) in boiling acetic acid. Reddish violet (when R=H) or blue-violet (when R=alkoxy) colour was initially developed on solution, but it almost discharged after *ca.* 6 h. Thioxanthylium perchlorates **6** (Y=S, R=H or alkoxy) were obtained by the action of perchloric acid on allenes **1** (Y=S, R=H or alkoxy). They were transformed into the corresponding thioxanthene-spiro-indenes **7** in boiling acetic acid in a relatively longer time (*ca.* 10 h).

Thioxanthylium perchlorates **6** (Y=S, X=ClO_4) gave back the corresponding allenes **1** (Y=S) quantitatively when heated in pyridine. On the other hand, reaction of xanthylium (or thioxanthylium) perchlorate **6** (Y=O or S, X=ClO_4, R=OMe) with methoxide anion in methanol yielded almost colourless crystals of 9-methoxy-9-[2,2-bis(*p*-methoxyphenyl)vinyl]-xanthene (or thioxanthene) **8** (Y=O or S, R=OMe). When dissolved in acetic acid, deep blue or blue-violet colour was developed, it being similar to that obtained on solution of the corresponding allene **1** in the same solvent. Measurements of electronic absorption spectra in the visible and UV. regions for solutions in acetic showed similar absorption maxima for both the allene **1** (Y=O or S, R=OMe) and the corresponding 9-methoxy derivative **8** (Y=O or S, R=OMe). This similarity suggests cleavage of the C-OMe bond at position 9 with acid to give the same species of xanthylium or thioxanthylium ions [4] [5], support for this being provided by formation mainly of the corresponding spiro-indenes **7** (Y=O or S, R=OMe) *via* xanthylium or thioxanthylium) acetates **6** (X=OAc) [1] on boiling solutions of 9-methoxy derivatives in acetic acid. Treating compounds **8** (Y=O or S, R=OMe) with perchloric acid gives the corresponding perchlorates **6** (Y=O or S, X=ClO_4).

On the other hand, reaction of 9-methoxy derivative **8** (Y=O or S) with equimolecular quantity of bromine afforded mainly the corresponding 2′-bromoindene **5** (Y=O or S, X=Br, R=OMe). Addition of bromine accompanied by development of similar deep colours. The formation of such bromoindenes is probably induced *via* a route involving addition of bromine to the double bond of **8** followed by spontaneous elimination of hydrogen bromide [6] [7] which readily cleave the C-OMe bond forming xanthylium (or thioxanthylium) bromide **3** (Y=O or S, X=Br) which cyclize to the corresponding 2′-bromo-spiro-indene **5**.

Reduction of allene **1** (Y=S) with zinc dust in acetic acid afforded the corresponding 9-(2,2-diarylvinyl)thioxanthene **2** (Y=S, X=H). This selective reduction probably *via* the thioxanthylium acetate **6** (Y=S, X=OAc) has been demonstrated by treatment of the perchlorate **6** (Y=S, X=ClO_4, R=OMe) with sodium borohydride to give compound **2** (Y=S, X=H, R=OMe).

Experimental Part

UV. spectra were measured with a *Beckman* DK-1 spectrophotometer, IR. spectra with a *Pye-Unicam* SP 1000 instrument, NMR. spectra with a *Varian* T 60 instrument and mass spectra with an *AEI* MS 9 spectrometer.

*6′-Substituted-3′-(*p*-substituted-phenyl)-thioxanthene-9-spiro-1′-indenes* **7**. When 9-(2,2-diarylvinylidene)thioxanthenes (**1**, 0.5 g) were dissolved in acetic acid (20 ml), a deep dark-red colour with the 2,2-diphenyl derivative and deep red-violet colour with 2,2-bis(*p*-alkoxyphenyl) derivatives were developed. Each solution was heated to boiling until the colour almost discharged (*ca.* 6 h). The mixture, diluted with cold water, was extracted with ether. The ether phase was washed (water, 5% Na_2CO_3-solution, water), dried (Na_2SO_4) and concentrated. The residue crystallized from methanol/ether to give the corresponding title compounds in *ca.* 90% yield.

In this manner were obtained: *3′-Phenyl-thioxanthene-9-spiro-1′-indene* (**7**, Y = S, R = H), m.p. 164°. – ^{1}H-NMR. (CCl_4): 7.06 (*s*, Ar) superimposed on 7.54–6.55 (*m*, 8 H, thioxanthene and 5 H, indene). – MS. (*m/z*): 374 (M^+).

$C_{27}H_{18}S$ (374) Calc. C 86.59 H 4.84 S 8.56% Found C 86.4 H 4.9 S 8.2%

*6′-Methoxy-3′-(*p*-methoxyphenyl)-thioxanthene-9-spiro-1′-indene (**7**, Y = S, R = OMe).* M.p. 156°. – ^{1}H-NMR. (CCl_4): 7.70–6.38 (*m*, 15 H, Ar, and 1 H–C(2′)); 3.72 and 3.52 (2 *s*, 6 H, 2 OCH_3). – MS. (*m/z*): 434 (M^+).

$C_{29}H_{22}O_2S$ (434) Calc. S 7.38% Found S 7.4%

*6′-Ethoxy-3′-(*p*-ethoxyphenyl)-thioxanthene-9-spiro-1′-indene* (**7**, Y = S, R = OEt). M.p. 145°. – MS. (*m/z*): 462 (M^+).

$C_{31}H_{26}O_2S$ (462) Calc. S 6.93% Found S 6.8%

*6′-Isopropoxy-3′-(*p*-isopropoxyphenyl)-thioxanthene-9-spiro-1′-indene* (**7**, Y = S, R = OiPr). M.p. 142°. – ^{1}H-NMR. ($CDCl_3$): 7.60–6.37 (*m*, 15 H, Ar and 1 H–C(2′)); 4.8–4.06 (2 overlapping *qa*, 2 H, $2(CH_3)_2CHO$–); 1.28 and 1.19 (2 overlapping *d*, *J* = 10 Hz, 12 H, $2(CH_3)_2CHO$–). – MS. (*m/z*): 490 (M^+).

$C_{33}H_{30}O_2S$ (490) Calc. S 6.54% Found S 6.7%

Reaction of compound **7** *with bromine.* Bromine (1 mmol) in $CHCl_3$ (2 ml) was added to the indenes **7** (1 mmol) in $CHCl_3$ (10 ml). The solvent was evaporated and the residue crystallized from methanol to give **5**.

2′-Bromo-3′-phenyl-xanthene-9-spiro-1′-indene (**5**, Y = O, X = Br, R = H). M.p. 140°.

$C_{27}H_{17}BrO$ (437) Calc. Br 18.2% Found Br 18.5%

*2′-Bromo-6′-methoxy-3′-(*p*-methoxyphenyl)-xanthene-9-spiro-1′-indene* (**5**, Y = O, X = Br, R = OMe). M.p. 176°. – ^{1}H-NMR. (CCl_4): 7.67–6.42 (*m*, 15 H, Ar); 3.71 and 3.53 (2 *s*, 6 H, 2 OCH_3).

$C_{29}H_{21}BrO_3$ (497) Calc. Br 16.07% Found Br 16.3%

*2′-Bromo-6′-ethoxy-3′-(*p*-ethoxyphenyl)-xanthene-9-spiro-1′-indene* (**5**, Y = O, X = Br, R = OEt). M.p. 163°. – ^{1}H-NMR. (CCl_4): 7.83–6.86 (*m*, 15 H, Ar); 4.43–3.77 (2 overlapping *qa*, 4 H, 2 OCH_2CH_3); 1.77–1.23 (2 overlapping *t*, 6 H, 2 OCH_2CH_3).

$C_{31}H_{25}BrO_3$ (525) Calc. Br 15.21% Found Br 15.5%

*2′-Bromo-6′-isopropoxy-3′-(*p*-isopropoxyphenyl)-xanthene-9-spiro-1′-indene* (**5**, Y = O, X = Br, R = OiPr). M.p. 149°.

$C_{33}H_{29}BrO_3$ (553) Calc. Br 14.44% Found Br 14.6%

*2′-Bromo-6′-methoxy-3′-(*p*-methoxyphenyl)-thioxanthene-9-spiro-1′-indene* (**5**, Y = S, X = Br, R = OMe). M.p. 156°.

$C_{29}H_{21}BrO_2S$ (513) Calc. Br 15.56 S 6.24% Found Br 15.2 S 6.4%

*2′-Bromo-6′-ethoxy-3′-(*p*-ethoxyphenyl)-thioxanthene-9-spiro-1′-indene* (**5**, Y = S, X = Br, R = OEt). M.p. 159°.

$C_{31}H_{25}BrO_2S$ (541) Calc. Br 14.78 S 5.92% Found Br 14.6 S 5.7%

*2'-Bromo-6'-isopropoxy-3'-(*p*-isopropoxyphenyl)-thioxanthene-9-spiro-1'-indene* (**5**, Y = S, X = Br, R = OiPr). M.p. 162°. - ^{1}H-NMR. ($CDCl_3$): 7.63-6.43 (*m*, 5 H, Ar); 4.83-4.06 (2 overlapping *qa*, 2 H, $2(CH_3)_2CHO-$); 1.36 and 1.23 (2 overlapping *d*, each *J* = 9 Hz, 12 H, $2(CH_3)_2CHO-$).

$C_{33}H_{29}BrO_2S$ (569) Calc. Br 14.03 S 5.63% Found Br 14.2 S 5.8%

Reaction of indenes 7 (Y = O or S, R = OMe) *with sulfuryl chloride.* Sulfuryl chloride (1 mmol) was added to a solution of each indene **7** (1 mmol) in CCl_4 (15 ml). The mixture was heated to boiling for 1 h, concentrated and the residue crystallized from methanol to give *2'-chloro-6'-methoxy-3'-(*p*-methoxyphenyl)-xanthene(*or *thioxanthene)-9-spiro-1'-indenes* **5** (Y = O or S, X = Cl, R = OMe), m.p. 175° and 181° respectively.

$C_{29}H_{21}ClO_3$ (452.5) Calc. Cl 7.84% Found Cl 7.4%
$C_{29}H_{21}ClO_2S$ (468.5) Calc. Cl 7.57 S 6.83% Found Cl 7.9 S 7.1%

*Reaction of bromine with 9-[2,2-bis(*p*-methoxyphenyl)vinylidene]xanthene(*or *thioxanthene)* **1**. - a) Bromine (1 mmol) in dried $CHCl_3$ (2 ml) was added to a solution of each allene in $CHCl_3$ (10 ml). Immediately a deep blue or blue-violet colour developed. On heating the mixture on the water-bath, HBr evolved. After removal of $CHCl_3$, the residue was crystallized from methanol to give the corresponding indenes **5** (Y = O or S, X = Br, R = OMe), m.p. (and mixed m.p.) 176 and 156° respectively. IR. spectra of each product was superimposable on that of a sample prepared above.

b) Repetition of experiment (a) with **1** (Y = O, R = OMe) (1 mmol) and the mixture left at RT. for 3 h. The deep bluish-black crystals of 2,2-bis(*p*-methoxyphenyl)-1,2-dibromo-2-(xanthen-9-ylium)ethylene bromide **4** (Y = O, X = Br, R = OMe) (yield 20%) were filtered off and washed with cold $CHCl_3$, m.p. 173-6° (dec.).

$C_{29}H_{23}Br_3O_3$ (659) Calc. Br 36.41% Found Br 36.7%

The solvent from combined filtrates was distilled off and the residue crystallized from methanol to give **5** (Y = O, X = Br, R = OMe).

Reaction of sulfuryl chloride with allenes **1** (Y = O or S, R = OMe). Sulfuryl chloride (1 mmol) was added to **1** (Y = O or S, R = OMe) (1 mmol) in CCl_4 (10 ml) and the deep blue mixture heated to boiling for 1 h. Then CCl_4 was distilled off, and the residue boiled for 30 min in methanol. The filtered solution was diluted with a few drops of ether and cooled to give *2'-chloro-6'-methoxy-3'-(*p*-methoxyphenyl)-xanthene(*or *thioxanthene)-9-spiro-1'-indenes* **5**, m.p. (and mixed m.p.) 175° and 181° respectively. IR. spectra were identical with those of the samples prepared above.

9-(2,2-Diarylvinyl)thioxanthylium perchlorate (**6**, Y = S, X = ClO_4). Perchloric acid (2 ml) (70%) was added to a cold solution of the corresponding vinylidenethioxanthene (1 g) in ether (50 ml), diluted with acetic acid (2 ml). The mixture was stirred for 30 min and the crystals formed were filtered off and washed with ether. Thus **6** were obtained in *ca.* 90% yield:

9-(2,2-Diphenylvinyl)thioxanthylium perchlorate (**6**, R = H). M.p. 182°. - UV. (λ_{max}, AcOH): 533, 379 and 278 nm.

$C_{27}H_{19}ClO_4S$ (474.5) Calc. Cl 7.47 S 6.75% Found Cl 7.2 S 6.6%

*9-[2,2-Bis(*p*-methoxyphenyl)vinyl]thioxanthylium perchlorate* (**6**, R = OMe). M.p. 160°. - UV. (λ_{max}, AcOH): 628, 475, 377 and 277 nm.

$C_{29}H_{23}ClO_6S$ (534.5) Calc. Cl 6.63 S 5.99% Found Cl 6.8 S 6.3%

*9-[2,2-Bis(*p*-ethoxyphenyl)vinyl]thioxanthylium perchlorate* (**6**, R = OEt). M.p. 173°.

$C_{31}H_{27}ClO_6S$ (562.5) Calc. Cl 6.30 S 5.69% Found Cl 6.4 S 5.9%

*9-[2,2-Bis(*p*-isopropoxyphenyl)vinyl]thioxanthylium perchlorate* (**6**, R = OiPr). M.p. 166°.

$C_{33}H_{31}ClO_6S$ (590.5) Calc. Cl 5.99 S 5.42% Found Cl 6.2 S 5.6%

Action of pyridine on perchlorates **6**. Allene **1** were quantitatively recovered by heating perchlorates **6** (0.5 g) in boiling pyridine (10 ml) for 10 min. Each solution was worked up (dilution with water, extraction with ether) to give after crystallization of the residue from methanol the corresponding allene. Thus were obtained: **1** (Y = S, R = H), m.p. and mixed m.p. (*cf.* [6]) 196°, **1** (Y = S, R = OMe), m.p. and mixed m.p. (*cf.* [6]) 124°, **1** (Y = S, R = OEt), m.p. and mixed m.p. 109°, and **1** (Y = S, R = OiPr), m.p. and mixed m.p. (*cf.* [6]) 123°.

Reduction of allenes **1** *with zinc dust.* To a warm deep blue-violet solution of the allene **1** (Y = S, R = OMe or OEt) (0.5 g) in acetic acid (15 ml), zinc dust (2 g) was added in small portions. The mixture was further heated until the colour become green (*ca.* 0.5 h), then filtered, cooled, diluted with water and extracted with ether. The ether phase was washed (water, 5% Na_2CO_3-solution and water), dried (Na_2SO_4) and evaporated. The residue crystallized from methanol to give: *9-[2,2-bis(*p*-methoxyphenyl)vinyl]thioxanthene* (**2**, Y = S, X = H, R = OMe), m.p. and mixed m.p. (*cf.* [6]) 134° and *9-[2,2-bis(*p*-ethoxyphenyl)vinyl]thioxanthene* (**2**, Y = S, X = H, R = OEt), m.p. and mixed m.p. (*cf.* [6]) 156° respectively in *ca.* 80% yield.

Reduction of perchlorate **6** (Y = S, X = ClO_4, R = OMe) *with sodium borohydride.* Sodium borohydride (0.2 g) was added in one portion to a cold stirred mixture of the violet perchlorate (0.5 g) in methanol (10 ml). The mixture was stirred for a further 10 min, diluted with water (2 ml) and the precipitate crystallized from methanol giving **2** (Y = S, X = H, R = OMe) as pale yellow crystals (yield 85%), m.p. and mixed m.p. (*cf.* [6]) 134°.

Reaction of perchlorates **6** (Y = O or S, R = OMe) *with sodium methoxide.* To a cold stirred solution of sodium methoxide in methanol (1 mmol Na in 10 ml MeOH) each perchlorate **6** (1 mmol) was added. Solution occurred with discharge of the colour. The mixture was stirred for a further 20 min then diluted with water and extracted with ether. The ether phase was washed with water, dried and evaporated. The residue was crystallized from methanol to obtain *9-methoxy-9-[2,2-bis(*p*-methoxyphenyl)vinyl]xanthene(*or *thioxanthene)* **8**, m.p. 147° and 140° respectively. - UV. (λ_{max}, AcOH): 624, 478, 370, 355 and 279 nm.

$C_{30}H_{26}O_4$ (450) Calc. C 80.00 H 5.77% Found C 79.9 H 5.9%

resp. UV. (λ_{max}, AcOH): 624, 478, 373 and 278 nm.

$C_{30}H_{26}O_3S$ (466) Calc. C 77.25 H 5.57% Found C 77.2 H 5.4%

Reactions of compounds **8** (Y = O or S, R = OMe). - a) *In acetic acid.* A solution of each compound **8** (0.5 g) in acetic acid (15 ml) was heated to boiling for 5 h. The deep colour first developed gradually faded. The solution was diluted with water and extracted with ether. The residue after evaporating the ether crystallized from ethanol/ether to give the corresponding spiroindenes **7**, m.p. and mixed m.p. 174° and 156° respectively.

b) *With bromine.* Bromine (1 mmol) in $CHCl_3$ (2 ml) were added to each solution of the 9-methoxy derivative **8** (1 mmol) in $CHCl_3$ (10 ml). A deep blue or blue-violet colour developed. $CHCl_3$ was evaporated and the residue crystallized from ethanol to yield the corresponding spiroindene **5** (Y = O or S, R = OMe), m.p. undepressed with authentic samples obtained as above.

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