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Studies on Xanthylium Salts. Behaviour of 9-Vinylidenexanthenes in Acid Media

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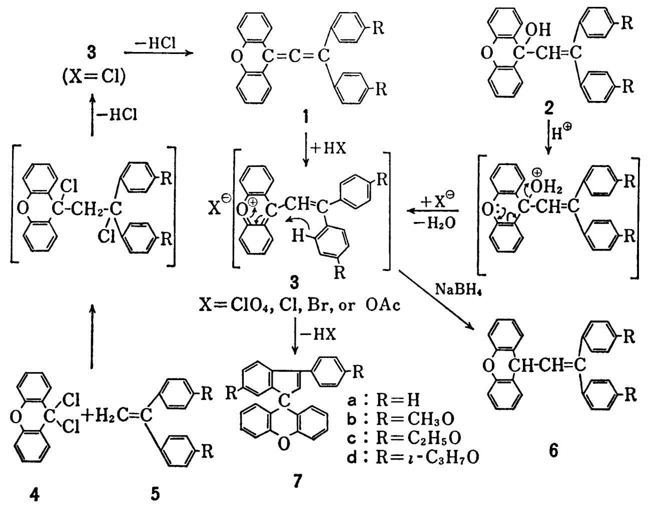
Unsymmetrical allenes namely, 1,1-diaryl-2-(9′-xanthenylidene)ethylenes (**1**) reacted readily with perchloric acid, hydrogen chloride, and acetic acid to give the corresponding highly coloured 9-vinylxanthylium salts (**3**). The latter derivatives (**3**) thermally rearranged in acid media to give spiro[indene-1,9′-xanthene]s (**7**). Structures of compounds **3** and **7** were established from chemical and spectral evidences. A new route for synthesis of allenes (**1**) was reported.

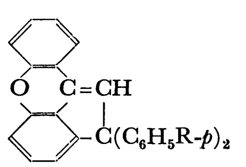
Orientation of polar addition of acids to substituted allenes to give carbonium ions has been shown to be controlled by the nature of substituents present.[1,2)] A study is now reported on the behaviour of unsymmetrical allenes[3,4)] (**1**) namely, 1,1-diaryl-2-(9′-xanthenylidene)ethylenes in acid media. These allenes (**1**, R= H, CH_3O, C_2H_5O, or *i*-C_3H_7O) added perchloric acid (in either acetic acid or methanol) to give crystalline, deeply coloured mono-perchlorate derivatives namely, 9′-[2,2-bis(*p*-substituted phenyl)vinyl]xanthylium perchlorates (**3**, R=H, CH_3O, C_2H_5O, or *i*-C_3H_7O; X= ClO_4). The structure of **3** (X=ClO_4) was established from analytical data and from the following findings: (i) The perchlorate **3** (R=H; X=ClO_4), derived from the corresponding allene (**1**, R=H), was identical with an authentic sample prepared by treatment of 1,1-diphenyl-2-(9′-hydroxy-9′-xanthenyl)ethylene (**2**, R= H) with perchloric acid in methanol at −5 °C; (ii) Reduction of perchlorate **3** (R=C_2H_5O; X=ClO_4) with sodium borohydride gave mainly 1,1-bis(*p*-ethoxyphenyl)-2-(9′-xanthenyl)ethylene (**6**, R=C_2H_5O); (iii) NMR spectrum of the *p*-alkoxy perchlorate **3** (R=*i*-C_3H_7O; X=ClO_4) revealed the equivalency of the 2,2-diaryl residues.

Allene **1** (R=H) added hydrogen chloride to yield deep red crystals of 9-(2,2-diphenylvinyl)xanthylium chloride (**3**, R=H; X=Cl). Synthesis of an authentic sample of **3** (R=H; X=Cl) was achieved by adding 9,9-dichloroxanthene (**4**) to 2,2-diphenylethylene (**5**, R=H). The reaction likely proceeded *via* an intermediate (scheme) which spontaneously eliminated hydrogen chloride on heating. The latter addition reaction was extended to prepare allenes **1** (R=H, CH_3O, C_2H_5O, or *i*-C_3H_7O) by using the appropriate ethylene (**5**, R=H, CH_3O, C_2H_5O, or *i*-C_3H_7O), and treatment of the intermediate products, without being isolated, with pyridine.

Electrophilic addition of hydrogen halides to substituted allenes has been reported to give monohalogenated products that were probably derived from vinylic cations formed by protonation of central carbon atom of these allenes.[1,2,5)] Selective addition of acids to π bond attached to xanthene residue of allenes (**1**) seemed to take place initially *via* a similar mechanism that followed by cyclic conjugation[6)] to give xanthylium derivatives (**3**). The deep colour of such perchlorates or chlorides (**3**, X=ClO_4 or Cl) in crystalline form or in solution might account for such conjugation. A similar chromophoric effect was noticed when colourless allenes (**1**) were dissolved in acetic acid (deep red, R=H, and bluish violet, R=alkoxy). This was probably due to similar type of protonation to give xanthylium acetate derivatives (**3**, X=OAc). UV spectra for both perchlorates (**3**, X=ClO_4) and acetates (**3**, X=OAc) were consistent with this observation.



Allenes **1** (R=H, CH_3O, C_2H_5O, or *i*-C_3H_7O) rearranged in boiling acetic acid to afford colourless crystalline products namely, 6-substituted-3-(*p*-substituted phenyl)spiro[indene-1,9′-xanthene]s (**7**, R=H or alkoxy). This rearrangement could also be brought about by heating a solution of allene **1** (R=H, CH_3O or C_2H_5O) in either ethanol containing hydrochloric acid or in ether saturated with hydrogen bromide. The reaction pathway for this rearrangement would require an initial formation of xanthylium ion intermediate (**3**, X=OAc, Cl, or Br) that cyclized through an internal electrophilic substitution[7,8)] of one of the 2,2-diaryl residues to give spiroindene (**7**). This was evidenced by: (i) the perchlorate **3** (R=H or C_2H_5O; X=ClO_4) converted in boiling acetic acid to yield typical indene **7** (R=H or C_2H_5O); (ii) 1,1-diphenyl-2-(9′-hydroxy-9′-xanthenyl)ethylene (**2**, R=H) cyclized in acid medium to give indene **7** (R=H), and (iii) NMR of *p*-alkoxy indenes (**7**, R=alkoxy) revealed the nonequivalency of the two *p*-alkoxyphenyl residues, and that one of them became trisubstituted. For example, the methoxyl groups of **7** (R=CH_3O) appeared as two singlets (δ, 3.71 and 3.53, each 3H), whereas the same groups were shown as overlapped singlet in the spectrum of each of the parent allene (**1**, R=CH_3O, δ, 3.90, 6H) and of 1,1-bis(*p*-methoxyphenyl)ethylene (**5**, R=CH_3O, δ, 3.75, s, 6H). The above findings were also in support of structure **7** for indenes rather than the alternative structure **8**. Furthermore, the latter **8**, by analogy with the behaviour of 9-xanthenylidene derivatives,[9,10] might be expected to add acids to give the corresponding xanthylium salt. This was not the case with our indenes; they failed to add acetic acid or perchloric acid and recovered mainly unchanged. Further relevant evidence was obtained from UV measurements in methanol or in acid medium (in acetic acid or in acetic acid/perchloric acid). Indene **7** (R=H) showed the same single absorption maximum at λ_{max} 290 nm in either solvent, whereas 9-benzylidenexanthene, as a reference example, showed: λ_{max} (CH_3OH) 341 nm; and λ_{max} (AcOH) 288, 336 nm; and λ_{max} (AcOH/$HClO_4$) 296, 384, 474, and 500 (shoulder) nm.



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Experimental

NMR spectra were measured with a Varian T 60 instrument and mass spectra with an A.E.I. MS9 spectrometer, and UV spectra with a Beckman DK-1 spectrophotometer. The infrared spectra were recorded with a Pye-Unicam SP 1000 spectrometer. All melting points were determined in open capillary tubes.

9,9-Dichloroxanthene (4). This was prepared by refluxing a solution of xanthone (2 g) in excess of thionyl chloride (10 ml) for 5 h. Excess thionyl chloride was recovered by distillation under reduced pressure. The residue obtained was mixed with 10 ml of petroleum ether (bp 60—80 °C), and the solvent was again removed under reduced pressure. The procedure was repeated for 5 times. All the processes were carried out under complete protection of moisture, and the final residue kept under dry conditions, mp 101—103 °C (lit, mp[11] 103 °C).[11]

1,1-Diaryl-2-(9-xanthenylidene)ethylene (1a—d). A mixture of 9,9-dichloroxanthene (prepared from 2 g xanthone) and 1,1-diphenylethylene (1.8 g) was heated on a steam bath for 2 h. The mixture was further heated in benzene for 15 min and filtered. The insoluble reddish-brown material, mp 155—157 °C (dec) showed no depression in mp when admixed with an authentic sample. The sample was prepared by passing hydrogen chloride for 10 min into a solution of 1,1-diphenyl(9-xanthenylidene)ethylene (**1a**, 0.5 g) in benzene (15 ml) and the deep red crystals formed were collected by filtration to give **3a** (X=Cl), mp 157 °C.

After a solution of **3a** (0.5 g) in pyridine (10 ml) had been refluxed for 10 min, water was added to the reaction mixture and worked up in the usual way. The product was recrystallized from methanol to give **1a**, mp and mixed mp[3] 205 °C in *ca.* 50% overall yield.

In the case of a mixture of 1,1-bis(*p*-alkoxyphenyl)ethylene (0.01 mol) and 9,9-dichloroxanthene (0.01 mol), extensive evolution of hydrogen chloride was observed on heating, and the reaction mixture was directly treated with pyridine and worked up to give 1,1-bis(*p*-alkoxyphenyl)-2-(9-xanthylidene)-ethylene (**1**): **1b**, mp and mixed mp[3] 125 °C; **1c**, mp and mixed mp[3] 125 °C; and **1d**, mp and mixed mp[3] 147 °C in *ca.* 40% yield. IR spectra of these allenes were superimposable with that of authentic samples. UV and visible spectra measurements which performed in glacial acetic acid showed for **1a**: λ_{max}: 515, 371, 346, 330, 257 nm and for **1b**: λ_{max}: 628, 478, 373, 355, 277 nm.

9-(2,2-Diarylvinyl)xanthylium Perchlorates (3a—d). Perchloric acid (2 ml, 70%) was added gradually to a stirred solution of 1,1-diaryl-2-(9-xanthenylidene)ethylene **1** (1.0 g) in either acetic acid or methanol (25 ml) and the mixture was further stirred for 30 min. The mixture diluted with ether and cooled to give the corresponding perchlorates **3a—d**, which separated as highly coloured crystals in *ca.* 90% yield. Thus were obtained: **3a**, mp 181 °C, λ_{max} (AcOH): 533, 380, 278 nm; Found: Cl, 7.8%. Calcd for $C_{27}H_{19}ClO_5$: Cl, 7.73%. This perchlorate (**3a**) could be prepared by adding perchloric acid (0.5 ml) to a cold solution (−5 °C) of compound (**2a**) (0.2 g) in methanol (25 ml). The mixture was stirred for 10 min and the red crystals deposited were collected by filtration, mp and mixed mp 181 °C.

3b, mp 170 °C, λ_{max} (AcOH): 612, 497, 367, 271 nm; Found: Cl, 6.9%. Calcd for $C_{29}H_{23}ClO_7$: Cl, 6.83%.

3c, mp 172 °C, λ_{max} (AcOH): 619, 490, 367, 271 nm; Found: Cl, 6.6%. Calcd for $C_{31}H_{27}ClO_7$: Cl, 6.48%.

3d, mp 157 °C, Found: Cl, 6.2%. Calcd for $C_{33}H_{31}ClO_7$ Cl, 6.17%.

Reduction of 9-(2,2-Diarylvinyl)xanthylium Perchlorates (3a, c). To a cold stirred suspension of each of the title compound (0.5 g) in methanol (10 ml), sodium borohydride (0.2 g) was added at once. The deep colour (red or blue violet) disappeared immediately and colourless crystals deposited. After stirring for 15 min, the mixture diluted with water (2 ml) was cooled and the solid precipitated was collected by filtration. It was crystallized from methanol to give the corresponding 1,1-diaryl-2-(9′-xanthenyl)ethylene (**6**) in *ca.* 90% yield. Thus were obtained: **6a**, mp and mixed mp[3] 164 °C and **6c**, mp and mixed mp[3] 115 °C.

Action of Pyridine on 9′-(2,2-Diarylvinyl)xanthylium Perchlorates (3). A solution of the perchlorate **3a—d** (1.0 g) in pyridine (10 ml) was heated to boiling for 10 min. The mixture diluted with water was extracted with ether. The ether phase was washed thoroughly with water, separated, dried ($MgSO_4$), and the solvent was distilled off. The residue crystallized from methanol, from which the allene (**1**) separated as colourless crystals in *ca.* 90% yield. Thus were obtained: **1a**, mp and mixed mp[3] 205 °C; **1b**, mp and mixed mp[3] 125 °C; **1c**, mp and mixed mp[3] 125 °C; and **1d**, mp and mixed mp[3] 147 °C.

*6-Substituted-3-(*p*-substituted phenyl)spiro[indene-1,9′-xanthene]s (7).* These compounds were obtained as follows: A solution of 1,1-diaryl-2-(9′-xanthenylidene)ethylene (0.5 g) in acetic acid (20 ml) was heated to boiling until the deep colour developed on dissolution (red in case of **1a**, and blue violet with **1b—d**) almost discharged (*ca.* 4 h). The solution was cooled, diluted with water and extracted with ether. The extract was washed successively with water, sodium carbonate solution (5%), and water and dried ($MgSO_4$). The residue obtained by evaporation of the solvent was crystallized from methanol to give colourless crystals of compound **7** in *ca.* 90% yield. Thus were obtained: **7a**, mp 174 °C, δ (CCl_4) 7.07 (s, C_6H_5) superimposed on 7.51—6.61 (m, 8H, of xanthene plus 3H, indene), *m/e* 358 (M^+); Found: C, 90.5; H, 5.1%. Calcd for $C_{27}H_{18}O$: C, 90.47; H, 5.06%. λ_{max} 290 nm (AcOH/Ac_2O, 9: 1, v/v) or in AcOH/Ac_2O/$HClO_4$ (70%) (9: 0.9: 0.1, v/v/v).

7b, mp 174 °C;[12] δ (CCl_4) 7.67—6.42 (m, 15H, Ar), 6.35 (s, 1H, indene H-2) and 3.71, 3.53 (2s, 6H, $2CH_3O$); *m/e* 418 (M^+); Found: C, 83.3; H, 5.4%. Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30%.

7c, mp 157 °C; δ (CCl_4) 7.58—6.46 (m, 15H, Ar), 6.41 (s, 1H, indene H-2), 3.94, 3.78 (2 overlapped q, *J*=8 Hz, each 2H of C_2H_5O), 1.38 and 1.24 (2 overlapped t, *J*=8 Hz, each 3H of C_2H_5O); *m/e* 446 (M^+); Found: C, 83.4; H, 5.8%. Calcd for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87%.

7d, mp 122 °C, *m/e* 474 (M^+); Found: C, 83.4; H, 6.4%. Calcd for $C_{33}H_{30}O_3$: C, 83.51; H, 6.37%.

When a solution of **3a** or **3c** (0.5 g) in acetic acid (20 ml) heated to boiling for 5 h and worked up as above, spiroindenes **7a**, mp and mixed mp 174 °C and **7c**, mp and mixed mp 157 °C were obtained respectively in *ca.* 80% yield.

To each solution of **1a** or **1c** (0.5 g) in ethanol (10 ml) concentrated hydrochloric acid (2 ml) was added. Each mixture was heated to boiling for 10 h. The colourless crystals separated on cooling the mixture were collected by filtration and were recrystallized from methanol to give the corresponding indenes **7a** and **7c**, mp and mixed mp 174 and 157 °C respectively.

Hydrogen bromide was bubbled in a cold ethereal solution of **1b** (0.5 g in 15 ml ether) until no more absorption of gas was observed. The mixture was refluxed for 30 min and left overnight. The solvent was recovered and the residue obtained was recrystallized from methanol to give **7b**, mp and mixed mp 174 °C.

9-Benzylxanthylium Perchlorate. To a cold solution of 9-benzylidenexanthene (0.5 g) in a mixture of acetic acid (4 ml)/acetic anhydride (1 ml), perchloric acid (70%, 0.5 ml) was added. The mixture was left for 30 min at room temperature and then was diluted with ether. The deep yellow crystals precipitated were collected by filtration and were washed with ether. They had mp 226 °C which showed no depression when admixed with an authentic sample of 9-benzylxanthylium perchlorate prepared from 9-benzyl-9-hydroxyanthene according to the procedure reported by Conant *et al.*;[13] λ_{max} 288, 336 nm ($AcOH/Ac_2O$, 9: 1 v/v) and λ_{max} 296, 384, 474, and 500 (shoulder) nm ($AcOH/Ac_2O/HClO_4$, 8.9: 1: 0.1 v/v/v) were shown in the spectra of 9-benzylidenexanthene. The same absorption maxima in acetic acid perchloric acid, were obtained when 9-benzylxanthylium perchlorate was measured in acetic acid.

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