

Unusual condensation of 2-(2-dimethylaminovinyl)-1-benzopyran-4-one with dimethyl acetylenedicarboxylate: formation of 2,3-bis(methoxycarbonyl)xanthen-9-one

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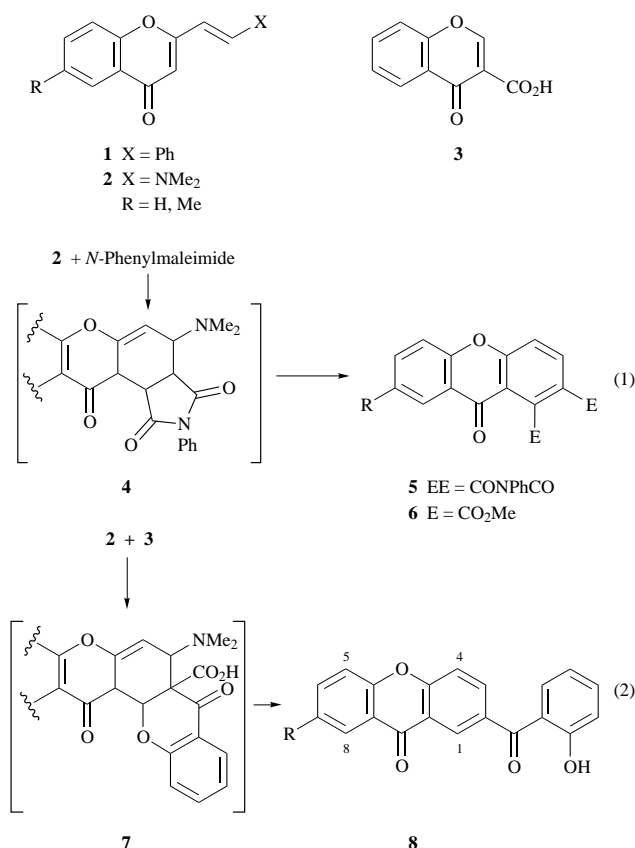
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Reaction of dienamine **2** (R = H and Me) with *N*-phenylmaleimide or chromone **3** gives xanthenes **5** and **8**, respectively, through initial [4 + 2] cycloaddition, whereas reaction with dimethyl acetylenedicarboxylate affords xanthone **13**.

The synthesis of xanthenes from 3-acyl-2-methyl-1-benzopyran-4-one (trivial name: 3-acyl-2-methylchromone)^{1,2} and particularly from some simple condensates of 2-methyl-^{3,4} and 3-formyl-2-methyl-chromone⁵ involving [4 + 2] cycloadditions has been of recent interest. Diels–Alder cycloaddition of (*E*)-2-styrylchromone **1** (R = H) with maleic anhydride and *N*-phenylmaleimide is always followed by a 1,3-hydrogen shift giving 1,2,3,4-tetrahydroxanthone derivatives.³ The title benzopyranone **2** (R = H and Me), because of its strong electron-releasing dimethylamino group, is obviously a more reactive diene than chromone **1** and is likely to undergo [4 + 2] cycloaddition even with moderately active dienophiles. Refluxing an equimolar mixture of the diene **2** and *N*-phenylmaleimide in DMF indeed produced the xanthone **5** evidently through the initially formed cycloadduct **4** which readily eliminated dimethylamine and was dehydrogenated under the reaction conditions [Scheme 1, eqn. (1)]. Chromone-3-carboxylic acid **3** however, is a weak dienophile, and only undergoes Diels–Alder reactions (unaided by any Lewis acid catalyst) with highly reactive Danishefsky dienes.⁶ Dienophile **3** reacted smoothly with the diene **2** in DMF under reflux indicating high diene activity of the latter, to give cycloadduct **7** (non-isolable) which, by decarboxylative pyran ring opening¹ and dedimethylation, was transformed into 2-salicyloylxanthone **8** [eqn. (2)]. **8** (R = H) was identical with an authentic sample.¹

Surprisingly, dimethyl acetylenedicarboxylate **9** did not behave like the two aforementioned dienophiles towards the diene **2**, and hence did not afford the cycloadduct **10** or its dedimethylaminated product **6** (Scheme 2, path a); instead, it gave exclusively the xanthone **13** isomeric with **6**. The formation of **13** may be rationalised as follows: compound **2** behaves like an unconjugated enamine in undergoing [2 + 2] cycloaddition with **9**, to give adduct **11** which isomerises to **12** (Scheme 2, path b).⁷ The ring opening of the cyclobutene **11** having both an acceptor and a donor substituent in an appropriate disposition, most probably occurs in a symmetry-allowed fashion,⁸ though involvement of an ionic mechanism with participation of the nitrogen lone pair of the dimethylamino group in the rearrangement (**11**→**12**) may not be completely ruled out.^{8,9} The ring-opened intermediate **12** incorporating a pre-existing double bond at the pyran 2,3-position, behaves as a hexatriene system which by electrocyclisation¹⁰ and subsequent elimination of dimethylamine affords the xanthone **13**.

The results presented here apparently reveal that the diene **2** undergoes Diels–Alder reaction with a relatively weak dienophile and [2 + 2] cycloaddition with a strongly reactive



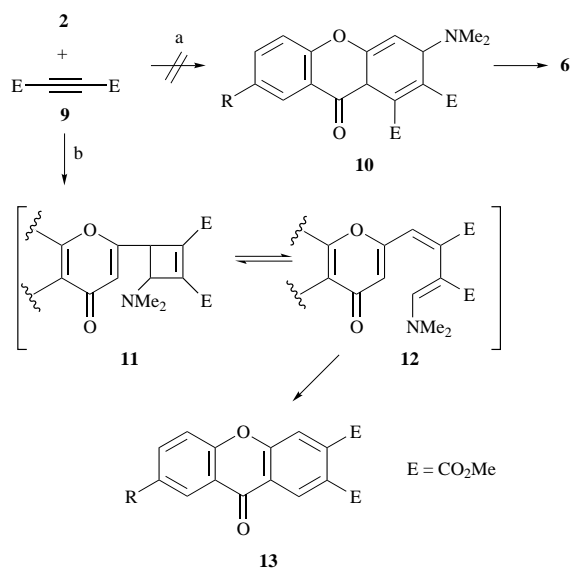
Scheme 1

one. It is known that double [2 + 2] cycloaddition predominates over [4 + 2] cycloaddition in the reaction of several 1-dialkylaminobutadienes with sulfene,¹¹ and this fact, together with the piece of work described in this communication, is a stimulus for further study of [4 + 2]- *vis-a-vis* [2 + 2]-cycloaddition of the diene **2** with different π bond systems of varying dienophilicity. Moreover, the formation of xanthenes or dihydroxanthenes through 2-(cyclobut-2-enyl)chromone intermediates like **11** deserves further study.

Experimental

General procedure for treatment of 2-(2-dimethylaminovinyl)-chromone **2** with *N*-phenylmaleimide, chromone-3-carboxylic acid and dimethyl acetylenedicarboxylate

A mixture of **2** (0.5 mmol) and either of the aforementioned dienophiles (0.5 mmol) in dimethylformamide (10 ml) was heated under reflux for 8 h. The reaction mixture was cooled and diluted with water. The precipitated solid was filtered off,



dried and crystallised from chloroform (charcoal)-light petroleum (bp 40–60 °C) to afford the product in 35–40% yield. The following compounds were prepared by this method.

N-Phenyl-9-oxo-9H-xanthene-1,2-dicarboximide 5 (R = H). Yellow solid, mp 252 °C (decomp.) (Found: C, 74.2; H, 2.8; N, 3.8. $C_{21}H_{11}NO_4$ requires C, 73.9; H, 3.2; N, 4.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1740 (amide CO), 1625 (xanthone CO); $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 8.39 (1 H, dd, $J_{8,1}$ 1.4, 8-H), 8.26 (1 H, d, $J_{8,4}$ 3-H), 7.91 (1 H, d, $J_{8,4}$ 4-H), 7.78 (1 H, dd, $J_{8,5}$ 8.3, 1.4, 6-H) and 7.61–7.30 (7 H, m, other ArH).

N-Phenyl-7-methyl-9-oxo-9H-xanthene-1,2-dicarboximide 5 (R = Me). Yellow solid, mp 254 °C (Found: C, 74.2; H, 3.5; N, 4.2. $C_{22}H_{13}NO_4$ requires C, 74.4; H, 3.7; N, 3.9%); δ_{H} 8.24 (1 H, d, $J_{8,4}$ 3-H), 8.14 (1 H, d, $J_{1,1}$ 1.1, 8-H), 7.89 (1 H, d, $J_{8,4}$ 4-H), 7.61–7.39 (7 H, m, other ArH) and 2.49 (3 H, s, Me).

7-Methyl-2-salicyloylxanthene-9-one 8 (R = Me). White crystals, mp 184 °C (Found: C, 76.2; H, 4.2. $C_{21}H_{14}O_4$ requires C, 76.4; H, 4.3%); δ_{H} 11.88 (1 H, s, exchangeable, OH), 8.68 (1 H, d, J_2 1-H), 8.14 (1 H, d, $J_{1,5}$ 8-H), 8.11 (1 H, d, $J_{8,7}$ 2.0, 3-H), 7.64 (1 H, d, $J_{8,7}$ 4-H), 7.63–6.93 (6 H, m, other ArH) and 2.50 (3 H, s, Me).

2,3-Bis(methoxycarbonyl)xanthene-9-one 13 (R = H). White crystals, mp 138 °C (Found: C, 65.2; H, 3.7. $C_{17}H_{12}O_6$ requires

C, 65.4; H, 3.9%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1745 (ester CO), 1735 (ester CO), 1670 (keto CO) and 1620 (C=C); δ_{H} 8.82 (1 H, s, 1-H), 8.33 (1 H, dd, J_8 1.3, 8-H), 7.78 (1 H, ddd, $J_{7,4}$ 6.9, 1.3, 6-H), 7.71 (1 H, s, 4-H), 7.53–7.40 (2 H, m, 5- and 7-H), 3.98 (3 H, s, CO_2Me) and 3.96 (3 H, s, CO_2Me).

2,3-Bis(methoxycarbonyl)-7-methylxanthene-9-one 13 (R = Me). White crystals, mp 166 °C (Found: C, 66.0; H, 4.2. $C_{18}H_{14}O_6$ requires C, 66.3; H, 4.3%); $\nu_{\max}/\text{cm}^{-1}$ 1740 (ester CO), 1730 (ester CO), 1675 (keto CO) and 1625 (C=C); δ_{H} 8.83 (1 H, s, 1-H), 8.11 (1 H, d, $J_{1,8}$ 8-H), 7.70 (1 H, s, 4-H), 7.58 (1 H, dd, $J_{8,4}$ 1.8, 6-H), 7.43 (1 H, d, $J_{8,4}$ 5-H), 3.98 (3 H, s, CO_2Me), 3.96 (3 H, s, CO_2Me) and 2.48 (3 H, s, 7-Me); δ_{C} 175.6, 167.2, 165.8, 157.0, 154.1, 138.6, 134.7, 125.4, 122.0, 121.1 (s), 136.6, 129.2, 125.9, 118.6, 117.7 (d), 53.0, 52.6 and 20.7 (q); m/z 326 (M^+ , 47%), 295 ($M - \text{OMe}$, 100), 236 (295 – $\text{OMe} - \text{CO}$, 7) and 208 (236 – CO , 11).

Acknowledgements

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† J Values are given in Hz